UNIVERSITY OF AGDER

Reactor design and characterization of biochar

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This master's thesis is carried out as a part of the education at the University of Agder and is therefore approved as a part of this education. However, this does not imply that the University answers for the methods that are used or the conclusions that are drawn.

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Preface

The use of coke in smelting plants has a problem, this problem is the CO_2 emissions to the atmosphere. Biochar obtained from biomass has taken more importance as a substitute of coke because it is more environmental friendly and it is a good way to reduce the greenhouse effect.

The motivation for this project is the use of biomass that is easily obtained from the environment to reduce the emissions of CO_2. It is also important the lack of industrial processes capable of producing biochar suitable for smelting plants.

Grimstad, June 2016.

Abstract

Biomass is considered to be a potential for the renewable energy sources in the future. Biomass has some advantages in front of fossil fuels like low sulphur and nitrogen content and it is a way to produce energy without contributing to greenhouse effect.

Biochar used as a chemical reducing agent in smelting plants needs specific characteristics such as a fixed carbon content higher than 85%, a volatile mater lower than 10% and a low ash content. The actual industrial processes are not enough to fulfil these conditions so a lab-scale study to adapt an actual industrial process to a system suitable to produce this kind of biochar will be made.

A bibliographic research will be done to determine which industrial process will be chosen and what kind of changes will be necessary to introduce to the reactor in order to produce biochar suitable for smelting plants. To determine the reactor dimensions a simulation in MATLAB will be done based on the heat transfer inside the reactor. Finally, a system to recover liquid and gas products will be also designed.

Future experiments will determine if this system is suitable for this kind of production or on the contrary, other characteristics or reactor type will be better choice than this one.

Acknowledgements

Firstly, I would like to thank my supervisor Henrik Kofoed Nielsen for his time and support throughout this project.

I would also like to thank Gerrit Surrup for his help and support during the thesis and Johan Olav and Maximilian Kink for their participation in the HAZOP.

This project has allowed me to know in more detail the biomass pyrolysis topic and to put engineering knowledge into practice.

Thanks to the University of Agder for letting me carry out the project in this university.

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1. Introduction

Charcoal has been used by mankind since the earliest time of civilization for different applications, for example the cave paintings, but in recent days the main uses of charcoal are as a fuel, a reducing agent in metal processing and for domestic purposes such as cooking. It is also used in the manufacture of several industrial chemicals like carbon tetrachloride, sodium cyanide and carbon disulphide **[1][2]**. The old process to obtain charcoal is known as charring and it is a chemical process of incomplete combustion of certain solids (vegetables) when they are expose to high heat. The remaining charcoal is composed primarily of carbon due to the remove of hydrogen and oxygen from the solid **[2]**.

The worldwide conscience regarding the effect of greenhouse gas emissions has caused that charcoal production needs to be more environmentally friendly and this leads to the "green charcoal" or biochar. Biochar is the word used to define the charcoal derived from renewable carbon-based resources (biomass) such as wood, nut shells, corn stover, rice straw, etc. A definition of biochar is the carbon-rich product obtained when biomass is heated in a closed container with absence of air, this process is known as pyrolysis and it produces biochar as well as produced gas and tar **[3]**. Biochar consists of elements such as carbon, hydrogen, sulphur, oxygen, nitrogen and minerals and it can be used for the same applications as charcoal. It is also useful as a way to improve the characteristics of the soils.

There are several processes to obtain biochar but this project is focused on pyrolysis. Pyrolysis is an irreversible thermal conversion process at elevated temperatures with the complete absence of an oxidant. Three products are obtained: non-condensable gases, condensable liquids (bio-oil) and biochar **[4]**.

The aim of this project is to design a lab-scale pyrolysis reactor to produce suitable biochar for being used as a reducing agent in metallurgic processes.

A reducing agent is an element or compound that loses an electron to another chemical species. The reaction of losing an electron and giving to another species is called redox. Reducing agents are important in the production of metals from their ores because most metals are found in the nature in chemical compounds **[5]**. Carbon, in the form of coke or biochar, is a valuable metallurgical reducing agent. An example of this reaction can be seen below in eq. 1.

$$SiO_2\ (s) + 2\ C\ (s) \rightarrow Si\ (l) + 2\ CO\ (g)\ \ \Delta H=859{,}4\ kJ/mol \qquad (1)$$

Nowadays, industrial processes are not good enough to produce biochar that can be used as a reducing agent in smelting plants, that's why a research of these processes will be done. A research of the best process conditions to obtain this kind of biochar will be also carried out.

After the information research, it has been seen that the current industrial processes characteristics to obtain biochar suitable for smelting plants are not the most appropriate, so some process changes will be required.

- What is the best temperature to obtain the desired biochar?
- What is the best heating rate to obtain the desired biochar?
- What kind of atmosphere is suitable for the process?
- What kind of biomass is more convenient?

Once the experimental parameters are set and the industrial process is chosen, it is necessary to introduce some changes in the reactor in order to hold the new process conditions.

- What changes are needed to repeat this process in lab-scale in order to have relevant experiments for later optimization of industrial scale?
- What is the best reactor type?
- What is the best material for the reactor?

Finally, it is necessary to design a system to recover the vapours produced during the pyrolysis in order to study or use them.

- What kind of system is the most appropriate to recover bio-oil and non-condensable gases for later study or usage?

2. Feedstock

This chapter is about a brief definition of biomass and its composition as well as the different analysis that can be carried out to determine some biomass properties and composition such as moisture content, ash content, volatile matter content, fixed carbon content, heating value and elemental composition.

2.1. Biomass

Biomass is a non-fossilized and biodegradable organic material obtained from plants, animals and microorganisms derived from biological sources. Biomass refers to wood, agricultural wastes, bagasse, industrial residues, municipal solid waste, sawdust, aquatic plants, among other materials **[6][7]**. The most common form of biomass resource is plant biomass from agricultural food production wastes and residues **[8]**.

The major components of biomass are cellulose, hemicellulose and lignin. These three components are decomposed at different temperatures, hemicellulose is the first to decompose followed by cellulose and finally the lignin **[6]**. Biomass composition has an important role in the pyrolysis process as it will be explained in chapter 3. Biomass also contains lipids, proteins, extractives, simple sugars, starches, ashes and other components **[6][7]**.

As a summary, Table 1 shows lignin, cellulose and hemicellulose content of some biomass feedstock.

Table 1. Lignin, cellulose and hemicellulose content of some biomass on a dry basis **[7]**.

Feedstock	Lignin (%)	Cellulose (%)	Hemicellulose (%)
Wood	25-30	35-50	20-30
Wheat straw	15-20	33-40	20-25
Switch grass	5-20	30-50	10-40
Sugarcane bagasse	23-32	19-24	32-48
Pinewood	27	40.7	26.9
Miscanthus	17	24	44
Corn stover	16-21	28	35
Hazelnut shell	42.9	28.8	30.4
Olive husk	48.4	24	23.6

Corncob	15	50.5	31
Tea waste	40	30.2	19.9
Rice straw	18	32.1	24
Cotton seed hairs	0	80-95	5-20

Biomass is considered as a renewable resource for energy production and there is a great quantity available around the world. Plants store sunlight as chemical energy through photosynthesis and then this energy is released by direct or indirect combustion as heat. Furthermore, biomass is the only renewable energy that can be converted into solid, liquid and gaseous fuel **[7]**.

Biomass is analysed by two ways, proximate and ultimate analysis. Proximate analysis determine the moisture content, volatile matter, ash content and fixed carbon present in the sample while ultimate analysis determine the mass fraction of the major constituents of the sample such as carbon, hydrogen, sulphur, nitrogen and oxygen.

2.2. Moisture content

The moisture content in biomass is the quantity of water in the material and it is expressed as a percentage of the material's weight. This weight can be referred to on a wet basis, on a dry basis or on a dry and ash free basis **[6][9][10]**. The formula is shown in the eq. 2 and 3.

$$MC_{wb} = \frac{H_2O\ weight}{wet\ weight} x100 \quad (2)$$

$$MC_{db} = \frac{H_2O\ weight}{dry\ weight} x100 \quad (3)$$

Where MC_{wb} is the moisture content on a wet basis and MC_{db} is the moisture content on a dry basis.

There are different methods to measure the moisture content in biomass. One of the standardized is described in Solid biofuels – Determination of moisture content – Oven dry method, EN 14774. The sample is dried in an air atmosphere oven using a temperature of 105 ˚C until constant weight to obtain dry biomass **[8][11]**.

2.3. Ash content

Ash is the inorganic incombustible part left after complete combustion of biomass and contains the mineral fraction. The major elements of ash are Ca, Si, Al, Ti, Fe, Mg, Na, K, S and P **[12]**. There are three factors that affect ash composition in plants, the plant type, the soil contamination and ash fraction **[12]**. On average, ash represents 0.5% in wood, 5-10% in agricultural crop materials and 30-40% in rice husks **[7][12]**.

Ash content are related with the heating value, high ash content of a plant makes it less desirable as fuel because an increase of 1% in ash concentration supposes a decrease of the heating value by 0.2 MJ/kg **[13]**. Another problem of ash is that high ash contents form slag and this may cause fouling problems and contaminate the metal in the smelting plants **[8]**.

Ash content can be measured on a wet, dry and dry and ash free basis and the expressions are shown in the eq. 4, 5 and 6 **[10]**.

$$AC_{wb} = \frac{ash\ weight}{wet\ weight} x100 \quad (4)$$

$$AC_{db} = \frac{ash\ weight}{dry\ weight} x100 \quad (5)$$

$$AC_{dafb} = \frac{ash\ weight}{dry\ and\ ash\ free\ weight} x100 \quad (6)$$

Where AC_{wb} is the ash content on a wet basis, AC_{db} is the ash content on a dry basis and AC_{dafb} is the ash content on a dry ash free basis.

The standard EN 14775:2009 can be followed to define the ash content **[14]**. The ash content is determined by calculation from the mass of the residue remaining after the sample is heated in air by the following process:

- Raise the temperature to 250 ˚C over a period of 30-50 minutes (heating rate of 4.5-7.5 ˚C/min) and maintain at this temperature during 60 minutes.
- Continue to increase the temperature to 550 ˚C over a period of 30 min (heating rate of 10 ˚C/min) and maintain at this temperature for minimum 120 minutes.

This project is focused on obtaining biochar suitable to work as a chemical reducing agent in metal processing. For this reason, the ash content has to be as low as possible **[15][16]**.

2.4. Volatile matter

Volatile matter is the part of biomass that is released as a gas or vapour when it is heated up to a certain temperature during certain time. The temperature and the time used to determine the volatile matter are reflected in EN 15148:2009. The dry sample is heated out of contact with ambient air at 900 ˚C for 7 minutes. Biomass normally has a volatile matter content of 70-86% in a dry basis **[10][17]**.

Volatile matter is formed by permanent gases such as CH_4, CO_2, CO and it is also formed by tar and other vapours which form the bio-oil after condensation **[18]**.

Volatile matter in biochar used to reduce metals has to be lower than 10% **[15][16]**.

2.5. Fixed carbon content

Fixed carbon (FC) is the remaining combustible material in a sample after the subtraction of moisture, ash and volatile matter. It is expressed as a percentage of the original material, so this can be translated to an equation like eq. 7.

$$FC = 100 – MC – AC – VM \quad (7)$$

Where FC is the fixed carbon content, MC is the moisture content, AC is the ash content and VM is the volatile matter.

The percentage of fixed carbon content in biochar that will be used as a chemical reducing agent in metal processing has to be higher than 85% **[15][16]**.

2.6. Elemental composition

The elemental composition of biomass is normally referred to the elemental carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O) present in the biomass. The quantity of each element varies from one type of biomass to other giving different characteristics to it. These elements are reported on a dry basis because the presence of moisture influences the quantity of hydrogen and oxygen, giving an extra amount of them **[18]**. Normally, oxygen content is calculated by difference.

Ultimate analysis determine the mass fraction of theses major constituents of the sample. Ultimate analysis is used with the calorific value to perform combustion calculations **[19]**.

Carbon and hydrogen are the most important elements of the biomass **[19]**. The carbon determination includes the organic carbon and any carbon present as mineral carbonate while the hydrogen determination includes the hydrogen from the organic materials, the moisture and the water from the hydration of silicates. Sulphur is an important parameter due to it is related with the SO_2 emissions that have an important environmental impact.

To carry these experiments, ISO 16948:2015 for the carbon, hydrogen and nitrogen content **[20]** and the ISO 16994:2015 for the sulphur content **[21]** are normally followed.

2.7. Heating value

Heating value or calorific value measures the energy content of the biomass that can be recovered during thermo-conversion (combustion) and it is measured using a bomb calorimeter **[8]**. Heating value is normally expressed as energy per kilogram of dry biomass (MJ/kg) and it is dependent on the presence of moisture in the biomass. A higher moisture content in the biomass implies a decrease of the heating value because part of the energy is used to evaporate the water.

Heating value can be expressed in two forms, higher heating value (HHV) and lower heating value (LHV). The difference between HHV and LHV depends on the assumption made on the final state of water. HHV considers that water is liquid in the final products so the latent heat of vaporization is included in the heating value. On the other hand, LHV consider that water remains as vapour in the final products so the latent heat of vaporization is not included **[10][22][23]**.

3. Thermal processes

Biomass is transformed into several components like gaseous, liquid and solid when it is exposed to heat. The process to obtain these products depends on the temperature, the heating rate, residence time and the presence of oxidant. Table 2 shows a classification of these processes.

Table 2. Biomass thermo-chemical conversion technologies and product weight distribution **[4]**

Thermal process	Amount of air used	Process temperature (˚C)	Gas (%)	Liquid (%)	Solid (%)
Torrefaction	No oxidant	200 – 320	60 – 75	3 – 5	10 – 35
Fast Pyrolysis (Bio-oil)	No oxidant	400 – 600	20 – 40	40 – 70	10 – 25
Slow Pyrolysis (Biochar)	No oxidant	300 – 700	40 – 75	0 – 15	20 – 50
Gasification	Incomplete amount of oxidant	500 – 1500	85 – 95	0 – 5	5 – 15
Combustion	Excess amount of oxidant	1000 - 1500	95	0	5

Gasification and combustion can be neglected due to the small biochar yield obtained in these processes, fact that is not interesting for this project. On the other hand, there is the pyrolysis that gives the highest biochar yield of all processes. Pyrolysis products and types are explained next.

Three different fractions are obtained after the biomass pyrolysis, gas, liquid and solid. The gas fraction is formed by the non-condensable gases while the condensable gases represent the liquid fraction or bio-oil after their condensation. Finally, the solid fraction is known as biochar. The composition of each one can vary depending on the experimental conditions but the main compounds of each product are:

- Biochar: amino, ketones, esters, aldehyde and carboxyl **[24]**
- Bio-oil: acids, esters, phenols, sugars, aldehydes, ketones and alcohols. **[25]**
- Non-condensable gases: CH_4, H_2O, H_2, CO and CO_2 **[26]**

Biochar obtained by pyrolysis and used as a chemical reducing agent in metal processing has some requirements such as a fixed carbon content higher than 85%, a volatile content less than 10% and an ash content lower than 5% **[15][16]**

3.1. Pyrolysis

Pyrolysis can be classified in two different processes, fast and slow pyrolysis. The product composition is different between them, this difference is mostly because of the heating rate and residence time.

3.1.1. Fast pyrolysis

The heating process is fast (over 100 ˚C/min) **[4]**. Fast pyrolysis is used to produce high bio-oil yield. Typically, the product obtained is formed of 40-70% of oily products, 10-25% of biochar and 20-40% of vapours **[4]**. The characteristics of fast pyrolysis are high heat transfer and heating rate, short vapour residence time, rapid cooling of vapours for high bio-oil yield and precision control of reaction temperature.

In fast pyrolysis the particle size used is small, a few millimetres. The bio-oil yield is decreased as the particle size is increased until a size of 1.5 mm **[27]**. Changes in the bio-oil yield are not observed for bigger particles **[27]**. This is due to the fact that the heat will never arrive to the centre of the particle and consequently the yields will decrease.

3.1.2. Slow pyrolysis

The heating process is performed normally at 1-30 ˚C/min for a temperature range of 300-700 ˚C **[28][29]**. The vapour residence time is high, this allows that some components of the vapour phase react with each other which results in the formation of biochar. Slow pyrolysis is used to produce biochar at low temperatures and low heating rates. The biochar yield obtained is about 35-50% **[30]**.

The particle size is not as important in slow pyrolysis as it is in fast pyrolysis, it can be small like in fast pyrolysis or bigger. It is important to establish the heating time according to the particle size in order to transfer the heat from the surface to the centre of the particles.

3.2. Factors affecting biochar yield

The final products composition obtained by pyrolysis is affected by several factors. The factors that affect the biochar yield are the biomass composition, temperature, heating rate, moisture content, particle size and vapour residence time.

3.2.1. Biomass composition

The most common biomass used for biochar production is wood. Wood is composed of hemicelluloses, cellulose, lignin, organic material and inorganic minerals, the percentage of each component is different between species. The amount of each component affects the biochar yield and mass loss **[1]**. The mechanism of conversion for hemicellulose, cellulose and lignin are explained next.

Lignin is an amorphous polymer composed of three phenylpropane units (p-hydroxyphenyl, guaicyl and syringyl) that contain a hydroxyl group in para position of the alkyl chain and they are connected by ether and carbon to carbon linkages **[31]**. The main conversion of lignin takes place in the temperature range between 200-450 ˚C and it is the responsible of the main release of primary volatiles **[1][31]**. The reactions responsible of this are mostly due to the instability of the propyl chains. After this step, conversion of the short substituents of the aromatic rings and a charring process (380-800 ˚C) produce low-weight incondensable gases and favour the char formation because of the rearrangement of the char skeleton in a polycyclic aromatic structure **[31]**. In a former study, it has been determined that higher yields of biochar involves a high lignin content **[32]**.

Cellulose is a linear homopolysaccharide of cellobiose monomers, composed of two β-glucopyranose units. The biggest weight change occurs between 300-390 ˚C and during this step the majority of the products are condensable organic compounds **[1][31]**. From 380-800 ˚C a charring process takes place **[31]**.

Finally, hemicelluloses are heteropolysaccharides with different composition depending on plant species **[31]**. The main conversion of hemicelluloses occurs between 200-350 ˚C and condensable and incondensable compounds are produced. For higher temperatures than 350 ˚C, the weight loss is linked to the rearrangement of the residue during the charring process. The char yield obtained is higher compared to cellulose **[1][31]**.

Hemicellulose, cellulose and lignin decomposition is shown in Figure 1.

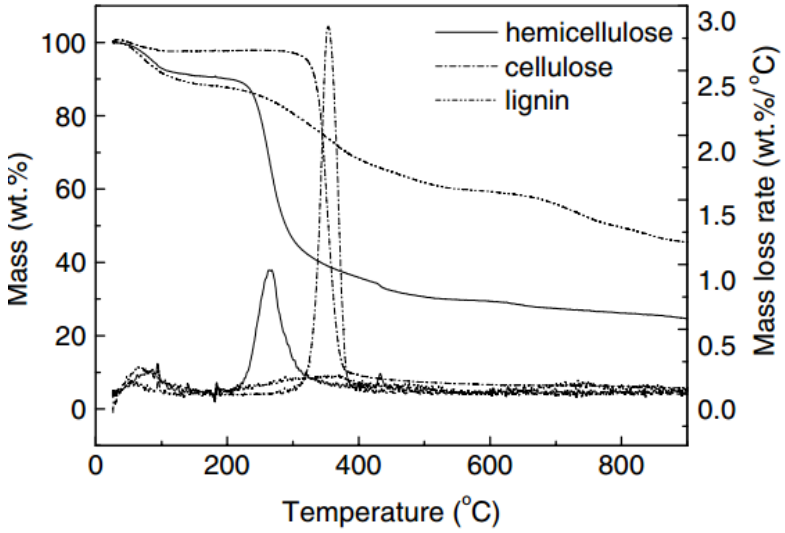

Figure 1. Pyrolysis curves of hemicellulose, cellulose and lignin in TGA (sample weight: 10 mg, heating rate: 10 ˚C/min, duration: 3 min, nitrogen flow rate: 120 ml/min) **[33]**.

Table 3 shows the yields obtained from individual fast pyrolysis (> 100 ˚C/min) of the biomass constituents with temperature between 500 and 800 ˚C.

Table 3. Biomass constituents yields (% of dry weight) with temperature between 500 and 800 ˚C from fast pyrolysis (> 100 ˚C/min)

	Char (%)	Tar (%)	Gas (%)	Water (%)
Cellulose	< 15	40-70	12-30	5-15
Hemicelluloses	20-30	20-35	22-35	20-30
Lignin	30-45	15-35	12-35	8-15

3.2.2. Temperature

The temperature is the most important factor affecting biochar yield. Biochar yield is decreasing while the temperature is increasing how it is shown in Figure 2. The optimum range to produce biochar yields above 25% is between 300-600 ˚C and for higher temperatures the biochar yield will decrease **[29][34][35][36]**.

Although the optimal range is 300-600 ˚C, in order to produce biochar with appropriate characteristics for metallurgical processes it is necessary a pyrolysis temperature of above 800 ˚C (Figure X) as well as low heating rates to reach the fixed carbon content of 85% **[15][16]**.

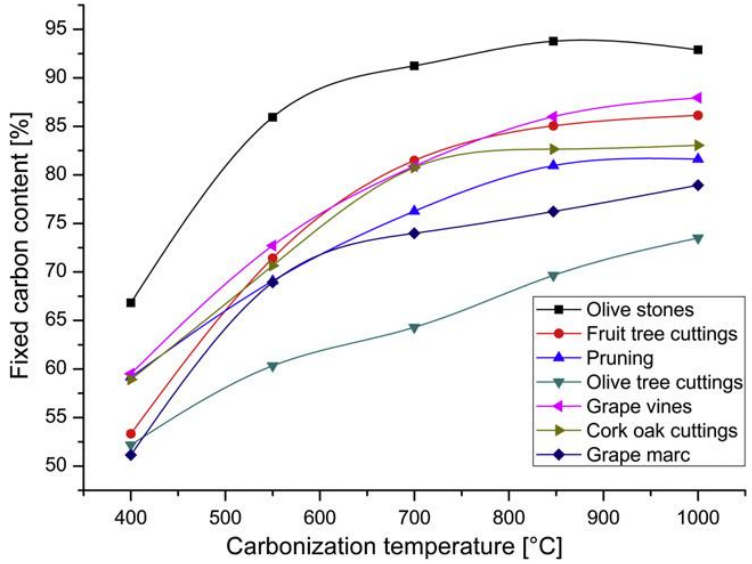

Figure 2. Fixed carbon content on a dry basis of the biomass at different temperatures **[15]**

Regarding the volatile matter content and ash content, if the temperature increases, the value of these two parameters decrease as it is shown in the experiments carried out by M.D. Huff. It can be observed that for an increase of temperature from 300 to 500 ˚C, the volatile matter decreases from 27.89 to 11.67% and the ash content from 4.93 to 2.37% **[37]**.

3.2.3. Heating rate

The heating rate is another important factor that affects biochar yield. Normally, biochar yield decreases when heating rate is increased **[35][38]**. As an example, the influence of the heating rate and temperature over the range from 300-600 ˚C is shown in Figure 3.

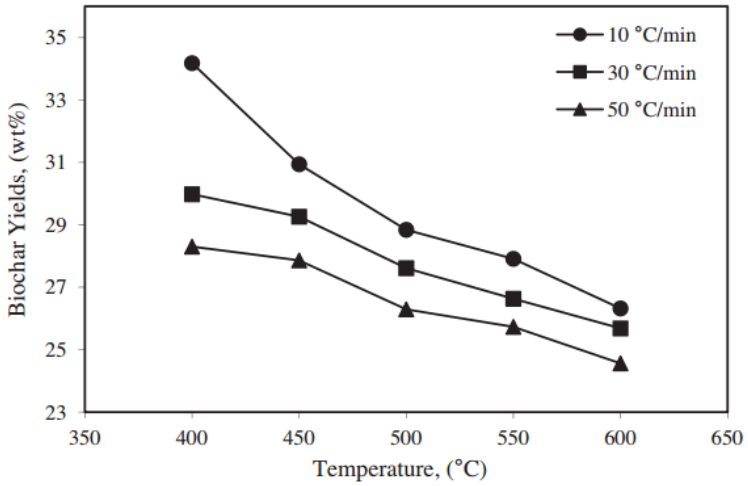

Figure 3. Effect of pyrolysis temperature and heating rate on biochar yield **[35]**.

The decreasing trend of biochar yield while the heating rate is increased can be appreciated, higher heating rates lead to low biochar yields.

In the previous section, it has been seen that temperatures above 800 ˚C are necessary to reach a fixed carbon content higher than 85%. Regarding the heating rate, low heating rates are needed to lower the tar amount and to increase the biochar output because due to high temperatures it is not really high.

3.2.4. Moisture content

Biomass moisture content affects the amount of biochar produced and the reaction time. If the biomass presents a high moisture content, more energy is required to dry the sample before any reaction occurs. It also slows down the cellulose degradation and increase the amount of biochar produced at high temperatures **[33]**. But, as it will be seen later, the moisture content it is limited depending on which kind of reactor it is used.

3.2.5. Particle size

As the particle size increases, the temperature gradients inside the particle are greater and the temperature in the centre of the particle is lower than on the surface. All this results in a higher biochar yield **[39]**.

Particle size used in fast pyrolysis is small, a few millimetres, because if the particle is bigger the heat will never arrive to the centre of the particle and consequently bio-oil yields will decrease **[27]**. In slow pyrolysis the particle size is not as important as it is in fast pyrolysis. The main concern is to fix a heating rate that allows heat to reach the centre of the particles.

As an example, Figure 4 shows the variation of biochar yield through temperature and particle size although these particle size values are normally used in fast pyrolysis more than in slow.

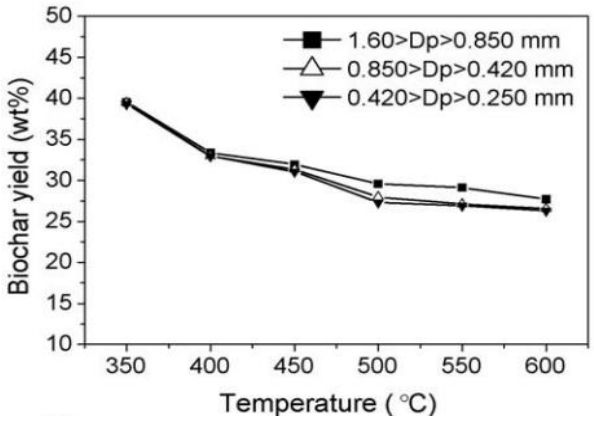

Figure 4. Particle size effect on biochar yield **[39]**.

3.2.6. Vapour residence time

During the pyrolysis process vapours are generated, these vapours consists of a condensable fraction (bio-oil) and a non-condensable fraction. The time that the gases spend inside the reactor affects biochar yield. As it is mentioned before, a higher vapour residence time allows the components in the vapour phase to react with each other and produce more biochar **[7]**. In slow pyrolysis the vapour residence time is normally greater than 5 seconds while in fast pyrolysis less than a second **[40]**.

Vapour residence time and biochar yield are related with the gas flow rate. If the inlet gas flow is increased the vapour residence time decreases and consequently the biochar yield too **[39]**. The Figure 5 shows the relation between the gas flow rate and the products yield.

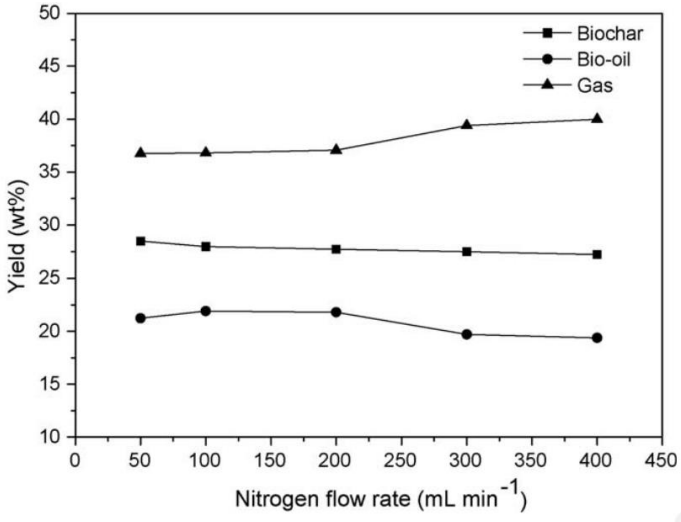

Figure 5. Gas flow rate effect on the product yields at 500 ˚C **[38]**.

4. Reactor

Pyrolysis process has been used for a long time. A review of traditional kilns and old retorts are presented next as well as some actual industrial processes. This project will select one of these processes to downscale it and make it useful to produce biochar for smelting plants.

4.1. Evolution of pyrolysis technologies

In the early stages of pyrolysis there was only one objective: produce biochar by wood carbonisation. The technologies used for this process have evolved from traditional methods to recent pyrolysis reactors. Some traditional methods to produce charcoal are describe in the following paragraphs.

The first reactor types are the earthmound kiln (Figure 6) focused on biochar production by slow pyrolysis and batch operation. Earthmound kilns are made of earth, sand and leaves that are used as an oxygen barrier. The size of these kilns is 2 m in diameter at the base and approximately 1.5 m high or they can be larger with a diameter up to 15 m **[41]**. They also have an opening at the top of 20 cm in diameter and six to ten air inlets are installed at the base.

This process works by lighting a fire which ignites the wood and then cover to avoid an excess in air flow inside the kiln. The wood diameter is approximately of 20 cm and the gaps between the logs are filled with smaller off-cuts to get a compact pile. There are some disadvantages such as the low charcoal yields, there is no control over the emissions and the airflow and earthmound kilns are not portable. This kind of reactors still has a great importance in Africa **[42]**.

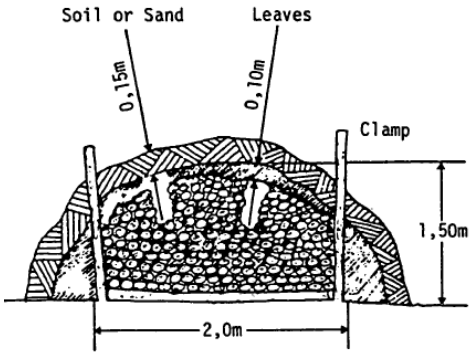

Figure 6. Earthmound kiln **[41]**.

Other kind of kilns are the sectional metal kilns. These kilns were important during war times, the army used them to produce charcoal for their own supply **[41]**. They consist of one cylindrical section with a conical cover and there are normally four air channels on the base. The kilns are made from sheet metal and their sections can be separated and carried to another site. A typical portable metal kiln is shown in Figure 7 with its usual dimensions.

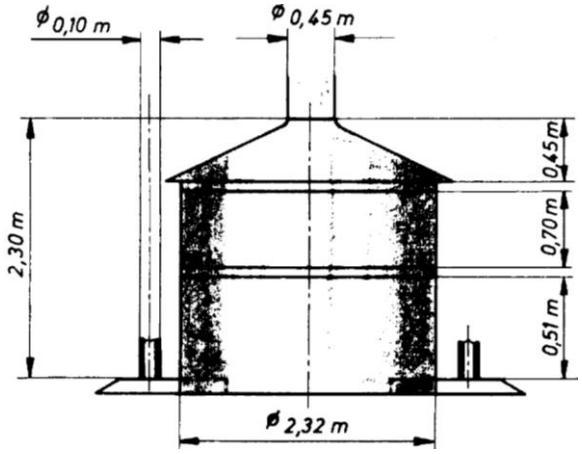

Figure 7. Portable metal kiln **[41]**

The maximum size of the wood is 60 cm in length and 20 cm in diameter, this size restriction is probably due to the difficulty of handle big wood logs. Fuelwood is usually placed horizontally making consecutive layers and it is recommended to put thicker logs in the centre of the kiln because they will not be as exposed to the heat as the ones close to the wall **[41]**.

At the end of eighteenth century, new technologies were designed to use the vapours obtained in the biomass pyrolysis. The appearance of the brick and concrete kilns had an important role in this field. Furthermore, this kind of reactors has more lifespan and better heat insulation than earthmound kilns.

An example of this kind of kilns is the Missouri kiln (Figure 8). It is a kiln made of concrete and reinforced steel capable of produce higher amount of biochar with higher quality than the two reactors mentioned before.

The volume of this kiln is normally of 180 m^3 and the walls have a thick of 25-30 cm. The thick of the walls is important to avoid cold spots due to the effect of the wind that can interfere with the process inside. The disadvantages are high costs of the materials and immobility of the reactor **[41][42]**.

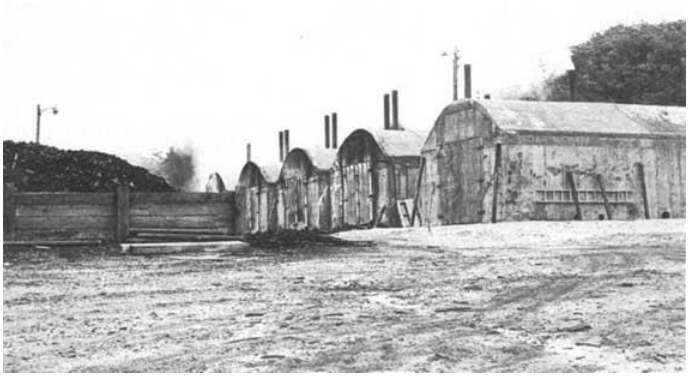

Figure 8. Missouri kilns **[43]**.

In the middle of the nineteenth century, the chemical industry brought to improve the system to collect the vapours from the carbonisation of the biomass, such as organic acids, methanol, acetone… due to this, iron retorts were designed. With this reactor it is possible to target the biochar, bio-oil and gases as a final product in a semi-batch operation mode.

Advances in this field have led to different ways to produce biochar, bio-oil and tar, one of which are the converters. While kilns are used to produce biochar in a traditional way, retorts and converter are industrial reactors designed to obtain biochar as well as products from volatile fraction. More precisely, converters produce biochar by carbonising small particles of biomass (chips and pellets) and retorts are used to pyrolyse larger particles (wood logs and pile-wood of a minimum length of 30 cm and maximum diameter of 18 cm) **[41][42]**.

Nowadays, there are several processes to obtain biochar. The most important are explained next.

The first one is the **Reichert retort process** (Figure 9). This process has been in commercial use for more than forty years and it consists of a metal retort (8.5 m length and 5 m diameter) with a raw material capacity of 100 m^3. This reactor is slowly heated by recirculating off-gases through a fixed bed of biomass. The raw material is wood with a maximum length of 30 cm and 10 cm thick to avoid the pressure drop over the biomass bed that restrict the gas circulation. The feedstock has a maximum moisture content of 20% **[41][42][44][45]**.

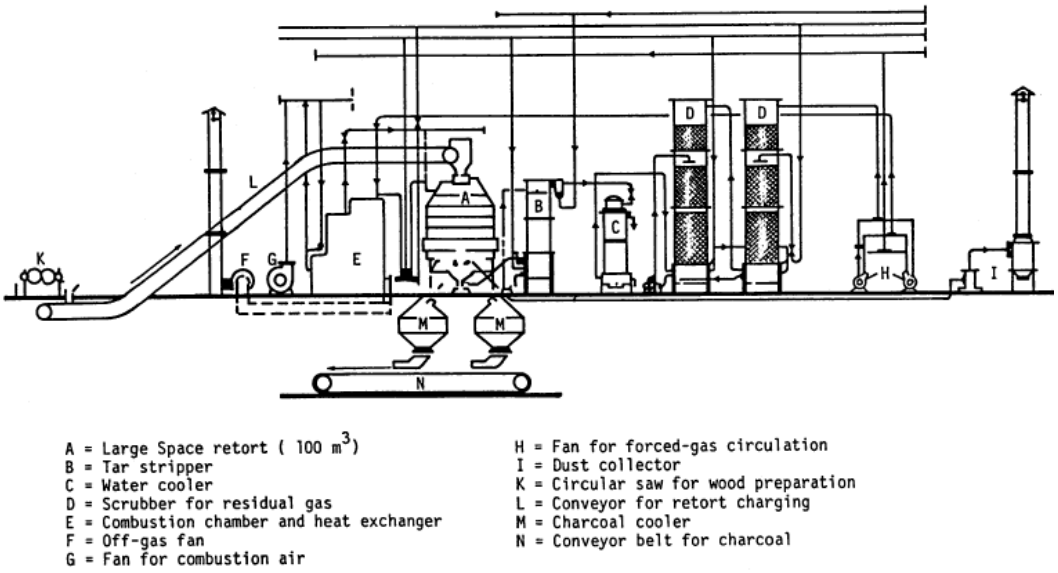

Figure 9. Reichert retort process **[41]**

Once wood is charged into the retort, the heating pipe is opened letting hot gases inside, the carbonization zone starts at the top and moves to the bottom. After this, the condensable gases are removed and the rest is sent into a chamber where is heated to 450-550 ˚C and recirculated as a hot gas afterwards. Finally, the biochar is discharged into a containers to cool it down with an average yield of 30-35 % **[41][42][45]**.

An advantage of this process is the possibility of working with multiple retorts so the off-gases from one retort can be used as hot gases for the next retort. This process is not widespread because of the high investments costs and the capital needed for the installation **[44][45]**

Other important process to obtain charcoal these days is the **Lambiotte process**. It is a continuous carbonisation process using a vertical cylinder of 18-33 m long and 3-6 m diameter (Figure 10) **[41][46]**, the wood particles have a size of 35 cm long and 10 cm diameter.

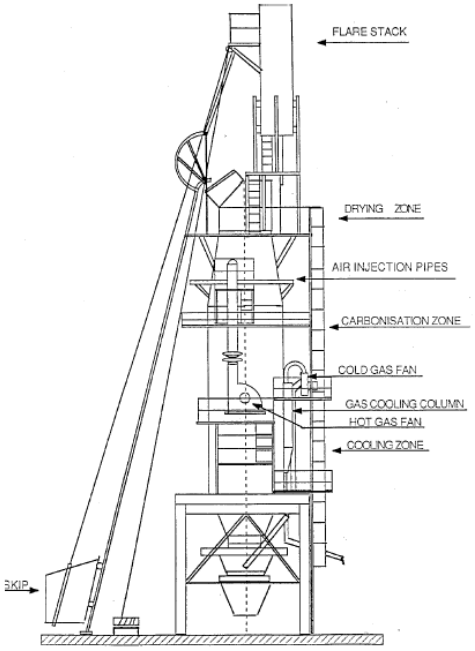

Figure 10. Lambiotte CISR retort **[46]**

Two different systems exist, the SIFIC and the CISR. In both systems, wood particles are introduced at the top and during their slow way down they cross three zones: drying zone, carbonisation zone and cooling zone. The two systems also have two closed gas-loops for the drying/carbonisation zone and the cooling zone **[41][42][46]**.

The SIFIC process can recover by-products. Vapours are taken out from the top of the retort and the condensable fraction is trapped in coolers before the gas combustion. A part of combustion gases is recirculated in the middle of the retort as a heating medium and the other part is cooled and introduced at the bottom to cool the charcoal **[42][46][47]**.

The CISR system is simpler because it does not recover by-products. The retort is heated by an internal system that burns part of the pyroligneous vapours and the lower part of the retort is cooled using another gas that is refrigerated and cooled in a scrubber **[42][46][47]**.

The temperature of the process is usually 400-500 ˚C and the maximum 800 ˚C, the moisture content of the feedstock has to be lower than 25% and a large particle size is required. The charcoal yield is approximately 30-35% **[41][48]**.

This process is probably the most efficient continuous wood pyrolysis and it has several advantages. It recirculates a part of the combustion gases as a heating and cooling medium, it is possible to obtain a high biochar yield (30-35%), it produces an homogeneous and controlled

quality product and it is suitable to produce large volumes of charcoal (6000 t/y) **[42][48]**. But it also has some disadvantages such as the need of having a moisture content lower than 25 % because an increased moisture content reduces the capacity, the vertical movement of the load causes fines formations and it is prone to corrosion by acetic acid. This can be solved using stainless steel or some material resistant to the corrosion **[49]**.

One of the most attractive designs is the **auger reactor** (Figure 11) **[38]**. This reactor can be heated externally or internally by hot gases and particle heat carrier. Biomass, chips or fine particles, is continuously fed into a screw filled with a heat carrier (if it is the case). Once the heat carrier and biomass are mixed, the system pushes the mix to the other side of the reactor where the vapours leave at the top and they are recollected into a condenser while the biochar and the heat carrier go to the bottom of the reactor. Afterwards, an extra process is required to separate the biomass from the heat carrier **[50][51][52][53]**.

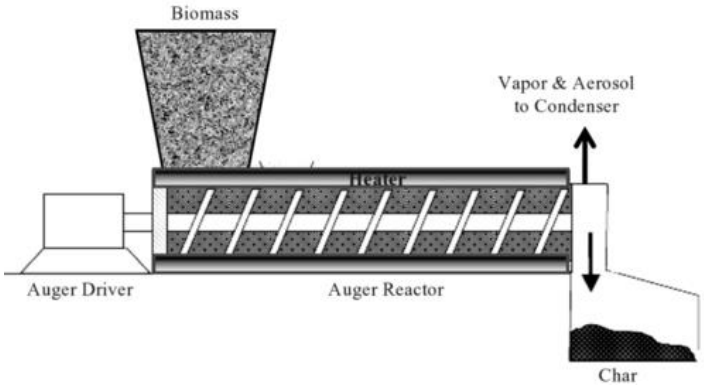

Figure 11. Auger reactor **[53]**

The reactor is normally made of metal, the temperature range used in this process is 400-800 ˚C and the residence time of the vapours is higher than in fluidised bed but lower than in slow pyrolysis. These allow to obtain more biochar due to the secondary reactions but the yield of bio-oil is lower than in the fluidised bed (60 %). The energy cost to run this process is usually lower than in other designs **[42][50][51]**.

This reactor has some disadvantages such as the mechanical wear, the plugging risk and the heat transfer presents limitations at large scale so the reactor size is generally small **[51][52]**.

The last system is the **Multiple Hearth furnace** (Figure 12). It consists of a vertical metal kiln with a several circular hearths one above the other and enclosed in a refractory-line steel shell. In the centre, there is a vertical rotating shaft with radial arms that drive the biomass (chips or

fine particles) from the top to the bottom hearth. Biomass crosses from one hearth to the other through a hole in each level. The system is typically used for slow pyrolysis and it is heated up by a hot gas which can be introduced at the bottom of the furnace or in each hearth through the side wall, the second option allows to set independently the temperature of each hearth. The yield of biochar obtained at the bottom of the reactor is about 25 % and this reactor can produced 18000 tons per year **[41][42][49][54]**.

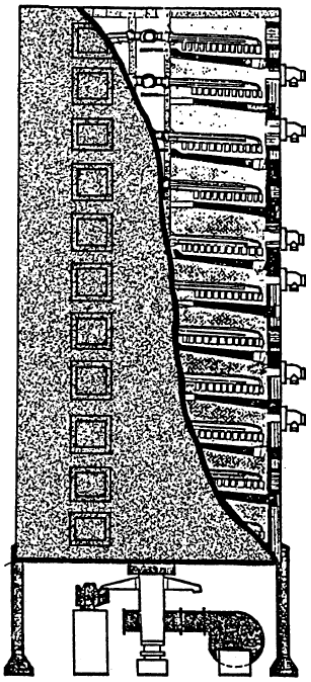

Figure 12. Multiple hearth furnace **[41]**

This reactor allows flexibility to handle a wide variety of materials and it also allows operational flexibility due to the control of the residence time, temperature in each hearth and the possibility of withdraw the gases from any hearth. Finally, different fuels (coal dust or waste oils) can be used in this reactor. Unfortunately, the cost of the reactor is high due to the complexity of the system to control each aspect of the process and high level maintenances are required **[41][49][54]**.

In the Table 4, there are the advantages and disadvantages of the four processes explained before.

Table 4. Advantages and disadvantages of biochar production processes

Process	Advantages	Disadvantages
Reichert retort	Possibility of multiple furnace Vapours are recirculated High biochar yield (30-35%)	High plant investment cost Moisture content below 20%
Lambiotte	Most efficient process Vapours are recirculated High biochar yield (30-35%)	Moisture content below 25% Vertical movement cause corrosion
Auger reactor	Good heat transfer Low energy cost	Low biochar yield Small particles Extra process to separate the heat carrier (if it is a particle type)
Multiple hearth furnace	Flexibility Elevated control of the process	High cost High maintenance

4.2. Pyrolyser design criteria

The objective of this project is to design a lab-scale reactor to obtain biochar as a chemical reducing agent in metal processing from the pyrolysis of pinewood, one of the most common biomass sources in Norway **[55]**. It has been seen that temperatures higher than 850 ˚C and slow heating rates are necessary. These characteristics differ from the ones currently used in the industry so after selecting an actual industrial reactor and the experimental parameters, it is necessary to select the suitable reactor characteristics and the correct operation mode based on these new conditions.

In order to choose the right properties, reactor types, operation modes, heating methods, materials, operational pressure, sealing types and different ways to control the process will be analysed.

4.2.1. Reactor type

4.2.1.1. Fixed bed reactor

A fixed bed reactor consists of a reactor with an immobile bed of feedstock. These reactors usually operate with long residence time, low gas velocity and high carbon conservation **[35][39]**. It is a suitable technology for small-scale. The problem of fixed bed reactors is the

removal of the tar.

Table 5 shows different studies reported in literature using a fixed bed reactor together with the temperatures, heating rates, gas flow rates and particle size used in the processes and Table 6 shows the resulting yields of fixed carbon, volatiles, ash, biochar and bio-oil of some of these studies.

Table 5. Recent studies on pyrolysis using a fixed bed reactor reported in literature

Reference	Pyrolysis type	Reactor type	Temp. (˚C)	Heating Rate (˚C/min)	Gas flow rate (L/min)	Particle size
Williams et al. (1996) **[38]**	Slow	Fixed bed (volume: 200 cm^3, stainless steel)	300-720	5-80	-	1 cm^3
Pütün et al. (2004) **[56]**	Slow	Fixed bed (volume: 350 ml, stainless steel 316)	400-650	5	0.05-0.4	0.224-1.8 mm
Özçimen et al. (2004) **[57]**	Slow	Fixed bed (diameter: 70 mm, length: 104 mm, stainless steel 316)	500	7	0.05-0.3	-
Sensöz et al. (2006) **[58]**	Slow	Fixed bed (diameter: 70 mm, length: 104 mm, stainless steel 316)	350-550	10, 50	-	0.425-1.8 mm
Ertas et al. (2010) **[39]**	Slow	Fixed bed (diameter: 80 mm, height: 35 cm, stainless steel)	350-600	10	0.05-0.4	0.25-1.6 mm
Xiao et al. (2010) **[59]**	Slow	Fixed bed (cylindrical, stainless steel)	300-700	5	0.35	-
Griessacher et al. **[15]**	Slow	Steel grid in a muffle	400-1000	5	0.87	3 mm
Chatterjee et al. (2013) **[60]**	Slow	Fixed bed (diameter: 110 mm, height: 390 mm, stainless steel 316)	500	10	10	0.425, 1 mm
Lee et al. (2013) **[61]**	Slow	Fixed bed (diameter: 10 cm, height: 30 cm, stainless steel)	300-700	10	1.5	< 1 mm
Angin et al. (2013) **[35]**	Slow	Fixed bed (diameter: 70 mm, length: 104 mm,	400-600	10, 30, 50	-	1.8 mm

		stainless steel 316)				
Masek et al. (2013) **[28]**	Slow	Fixed bed (quartz glass reactor tube, diameter: 50 mm)	200-350	5	0.33	-
Park et al. (2014) **[29]**	Slow	Fixed bed (diameter: 10 cm, height: 30 cm, stainless steel)	300-700	10	1.5	-
M.D. Huff et al. (2014) **[37]**	Slow	500 cm^3 hastelloy autoclave high pressure batch reactor	300-500	12	-	1-2 cm

Table 6. Volatile matter, fixed carbon, ash and biochar and bio-oil yields on a dry basis of different studies

Reference	Biomass	Volatile matter (%)	Fixed Carbon (%)	Ash (%)	Biochar yield (%)	Bio-oil yield (%)
Özçimen et al. (2004) **[57]**	Rapeseed cake	18.7	63.7	17.6	27.4	59.7
Griessacher et al. **[15]**	Olive stones	-	66-93.8	-	23-39	-
	Grape vines		60-87		27-43	
	Cork oak		58-85		26-42	
	Pruning		58-81		27-41	
Lee et al. (2013) **[61]**	Bagasse	9.17	80.97	8.57	24.5	55.1
	Cocopeat	14.3	67.25	15.9	38.7	39.1
	Paddy straw	6.46	39.1	52.37	41.0	37.2
	PKS	12.29	80.85	6.86	32.2	51.4
	Wood stem	12.79	83.47	2.28	22.3	59.5
	Wood bark	18.14	68.66	12.84	31.9	50.5
Angin et al. (2013) **[35]**	Safflower seed cake	9.8-25.2	67.3-80.7	7.5-9.5	25-34	-
Park et al. (2014) **[29]**	Rice straw	5.88-34.54	28.06-39.52	37.4-54.6	26-50.2	32-43.3
M.D. Huff et al. (2014) **[37]**	Pine 300 ºC	27.89	67.18	4.93	32.89	-
	Pine 400 ºC	19.57	76.44	3.99	27.26	
	Pine 500 ºC	11.67	82.11	2.37	26.47	

4.2.1.2. Fluidised bed reactor

Fluidised bed reactors are popular for fast pyrolysis as they provide rapid heat transfer, good control for pyrolysis reaction and vapour residence time, extensive high surface area contact between fluid and solid per unit bed volume, good thermal transport inside the system and high relative velocity between the fluid and solid phase **[7]**. This kind of reactors is mostly used to produce bio-oil by fast pyrolysis however some experiments have been done to produce biochar in fluidised bed. For example, two studies obtained biochar using fluidised bed reactor with a yield of 31% (500 ˚C and fast pyrolysis) **[62]** and 19% (500 ˚C and fast pyrolysis) **[63]**. Bridgwater, Meier and Radlein (1999) studied the most suitable particle size for bio-oil production through pyrolysis. They reported that the appropriate size is less than 1 mm and particles less than 2 mm can be used in fast pyrolysis in a fluidised bed **[64]**.

Table 7 shows different studies using a fluidised bed reactor.

Table 7. Recent studies on pyrolysis using a fluidised bed reactor reported in literature

Reference	Pyrolysis type	Reactor type	Temp. (˚C)	Particle size (mm)	Gas flow rate/ Residence time	Biochar yield (%)	Bio-oil yield (%)
Heo et al. (2010) **[65]**	Fast	Fluidised bed (diameter: 80 mm, height: 300 mm, stainless steel 306)	350-550	0.3-1.3	5 L/min	12.1-32.4	60-69.2
Bok et al. (2013) **[66]**	Fast	Fluidised bed (rectangular, 300x75x300 mm, stainless steel 316)	400-550	1-2	70 L/min	15-30	40-48
Bok et al. (2013) **[66]**	Fast	Fluidised bed (diameter: 100 mm, height: 300 mm, stainless steel 316)	400-550	1-2	30 L/min	20-28	45-50
Kim et al. (2014) **[67]**	Fast	Fluidised bed (diameter: 35 mm, height: 400 mm, stainless steel 316)	350-500	-	1.2-3.8 s	17.1-20.9	47.4-57.2
Hwang et al. (2016) **[68]**	Fast	Fluidised bed (diameter: 100 mm, height: 300 mm)	400-550	1-2	0.8 s	20-29	48-51
Hwang et al. (2016) **[68]**	Fast	Fluidised bed (rectangular, 300x75x300 mm)	400-550	1-2	1.6 s	17-30	39-50

4.2.1.3. Ablative reactor

Biomass is pressed against a heated reactor wall using mechanical pressure. Biomass melts in contact with the wall and the residual oil evaporates giving place to pyrolysis vapours **[42]**. Some advantages of these reactors are that the feed material does not require excessive grinding and the process allows much larger biomass particle size than other types of pyrolysis reactors **[42]**.

4.2.1.4. Rotating cone reactor

Rotating cone reactors mix the biomass with hot sand to generate the pyrolysis reaction. Vapours are condensed in a condenser while biochar and sand are sent to a combustor. The sand is heated again and recirculated at the base of the cone. This kind of reactors produces high bio-oil yield **[42]**.

4.2.2. Operation mode

4.2.2.1. Batch operation

The main focus of this mode is to produce biochar leaving aside the production of the byproducts. This process consist of two stages, heat up the biomass followed by a cool down period. After the cool down period the product can be discharged. The volatiles formed during the process are normally released to the atmosphere. Batch operations is a common practice in small reactors **[42]**.

4.2.2.2. Semi-batch operation

The difference between semi-batch and batch operation is the use of the vapours as a heat source between batch reactors. The operating process is showed in Figure 13.

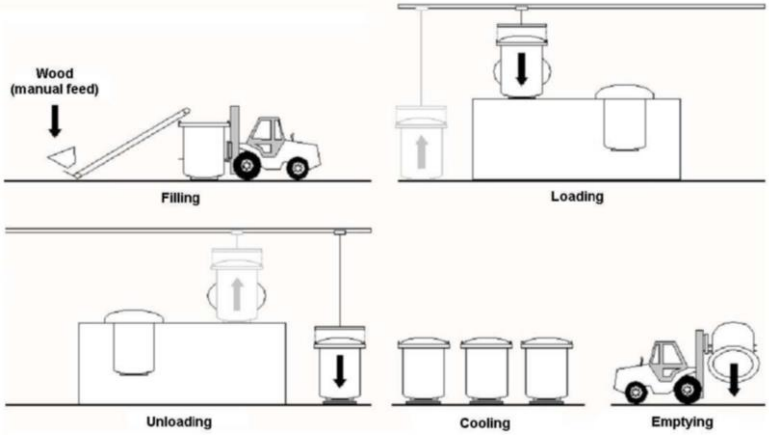

Figure 13. Semi-batch process **[42]**.

4.2.2.3. Continuous operation

This operation system is designed to work in a continuous way. It is only allowed to stop during maintenance tasks. This system has shown that is suitable for a large-scale production. An example would be a continuous wagon reactor.

4.2.3. Heating method

4.2.3.1. Auto-thermal

Partial combustion or auto-thermal of pyrolysis vapours and biochar is the most common method for small-scale processes. The method consists of burning part of the raw material with controlled air inlet that provides the energy necessary for the process.

4.2.3.2. Indirect heating

The reactor is heated from the outside. The heat is transferred to the feedstock through the reactor walls. The biomass is sealed inside the reactor and heated up with external heat that cause the pyrolysis.

The most common choice of indirect heating is the use of a furnace. This decision allows to have more control of the process **[15][34][61]**

4.2.3.3. Contact with hot gases

The heating process is carried out by direct contact between the feedstock and hot gases. This reduces the need for expensive heat transfer surfaces but there are costs associated with the heating of the gases. This method is suitable medium to large scale.

4.2.3.4. Contact with solid heat carrier

A solid material is used to transfer heat to the biomass. Sand, metal or ceramic balls are used as a solid heat carrier. The contact between the heat carrier and biomass intensifies heat transfer, facilitates rapid heat rates and improves pyrolysis process efficiency. In some designs, the heat carrier media can act as a tar cracking catalyst, improving the quality of the pyrolysis gas. The solid is heated up by the combustion of pyrolysis co-products or other fuels.

4.2.4. Materials

The first kilns and retorts were made of earth and concrete due to the availability and the low cost of this materials.

Earth is used to avoid the entrance of oxygen in the kiln and to insulate the recipient. It is an available, low cost and non-combustible material. Although it is used as an insulating material, there is still losses of heat **[1]**. Concrete or reinforced concrete is a better sealant and insulating than the earth. Moreover, this material increase the lifespan of the reactor. A disadvantage of concrete is that it doesn't resist high temperatures, when the material reaches these temperatures it presents fractures **[1]**.

Two of the most common materials are the ceramic materials and metals. However, only a little group inside these materials can be used as a reactor material under the new conditions described before.

4.2.4.1. Ceramic

Ceramics are chemical compounds formed by metals and non-metals, mostly oxides, nitrides and carbides. Due to this, the atomic bonding in these materials are very strong and can be ionic, covalent or a combination of the two. As a consequence, ceramics have a high melting point and a relatively low electrical conductivity **[69]**.

Ceramic materials have excellent strength to compression but they have a low tensile strength because of the surface flaws which have a weakening effect. The modulus of elasticity of ceramics can be quite high, this expresses stiffness (the ability of a material to resist deformation under stress), and this modulus in combination with low density makes ceramics a useful material for structures where weight reduction is important **[70]**. Another consequence of the strong interatomic bonding is that ceramics are hard and strong, they resist penetration by scratching or indentation and they can be used as abrasive particles for metal removal, but they

are brittle **[69][70]**.

Ceramic materials have low coefficients of thermal expansion and they are not good heat conductors. A disadvantage of this is that ceramics are susceptible to thermal shock that can cause the appearance of cracks when they are subjected to temperature changes. Ceramics have low chemical reactivity when exposed to oxidizing environments at high temperatures **[70][71]**.

It is possible to classify the ceramics using chemical composition as a basis, the categories are:

- Oxides (alumina, Al_2O_3; magnesia, MgO; zirconia, ZrO_2)
- Carbides (silicon carbide, SiC; silicon nitride, Si_3N_4; boron nitride, BN)
- Silicates (silica, SiO_2; forsterite, Mg_2SiO_4; kaolinite clay, $Al_2(Si_2O_5)(OH)_4$)
- Glass Ceramics.

Ceramics are not easy to produce and they are not useful for a single test cylinder so this material is not going to be considered as a possibility for the reactor material. Another reason is the fact that the reactor will be heated externally by a furnace so it is needed a material with high values of heat conductivity but ceramics has normally low values **[69][70][71][72]**.

4.2.4.2. Metal alloys

Metals are pure elements which give up electrons to form metallic bonds. Pure metals have limited applications due to their definite properties. When two or more pure metals are melted together to form a new metal with different properties from the original metals, it is called an alloy.

Metal alloys are divided in two groups, ferrous and nonferrous. Iron is the main constituent of the ferrous alloys while nonferrous alloys are not iron based. Figure 14 shows the classification for metal alloys.

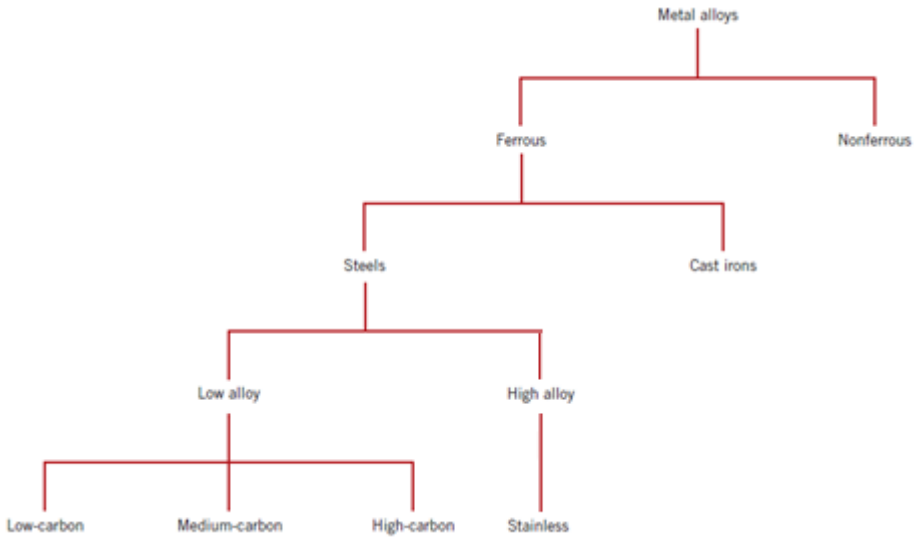

Figure 14. Classification for metal alloys **[69]**

Nonferrous metals are metals, including alloys, which do not contain iron in considerable quantity. These metals are used for desirable qualities such as low weight, higher conductivity or resistance to corrosion but they are generally more expensive than ferrous metals. Most important nonferrous metals are aluminium, copper, lead, nickel, titanium and zinc **[69][70]**.

Ferrous alloys are produced in larger quantities than any other metal because compounds that contains iron exist in abundant quantities, metallic iron and steel alloys can be produced in an economical way and ferrous alloys are extremely versatile. Some disadvantage of this type of metal alloy are the corrosion and the high density. Ferrous alloys are divided in steels and cast irons. Steels are iron-carbon alloys that may contain others alloying elements, reason for what exist thousands different types **[69][70]**.

Carbon is the most common alloying element in the iron which significantly affects the structure and properties of iron. It exists an iron-iron carbide phase diagram (Figure 15) that represents the different phases present for a given alloy composition and temperature. It is normally studied up to 6.67% carbon because iron alloys of practical industrial importance contain no more than 5% carbon. The most common steels are classified according to carbon concentration in low, medium, high carbon types and stainless steel **[69][70]**

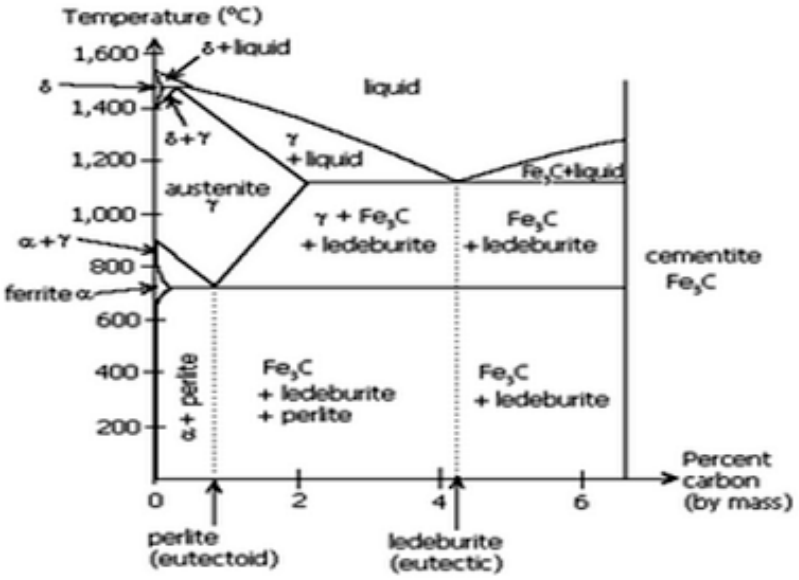

Figure 15. Iron-Iron Carbide phase diagram **[73]**

A classification on carbon basis and discussion of each type of ferrous alloy is presented next.

Cast iron

It is a class of ferrous alloy with a carbon content above of 2 % but, normally, it presents a range of carbon content between 3.0-4.5 %, this value implies that for most cast irons, carbon is presented as graphite. Cast iron also contains more than 1 % silicon **[69][70][74]**.

Cast irons have a low melting temperature as it is shown in the phase diagram. Alloys with a carbon content of 3-4.5 % are completely liquid at approximately 1150-1200 ˚C, which is lower than for steels. They don't have a good resistance against oxidation and the thermal conductivity is lower than for steel.

The most common cast iron are white, gray, nodular, malleable and compacted graphite **[74][75]**.

- White cast iron contains less than 1.0 % silicon and it is extremely hard but very brittle. It is used for applications that need a very hard and wear-resistant surface.
- Gray cast iron contains between 1.0-3.0 % silicon. It is weak and brittle in tension but under compressive stress, strength and ductility are much higher.
- Nodular iron consists in adding a small amount of magnesium and/or cerium to gray iron to change the properties. It is stronger and more ductile than gray iron.

- Malleable iron consist in heating white iron at temperatures between 800-900 ˚C for a certain time period in a neutral atmosphere. The result is higher strength and ductility.
- Compacted graphite iron is the most recent cast iron. Carbon content is between 3.1-4.0 %, silicon content 1.7-3.0% and it also contains magnesium and/or cerium but in lower concentration than nodular iron. This cast iron has good strength and ductility and compared to the other cast iron, it has higher thermal conductivity, better resistance to thermal shock and lower oxidation at high temperatures.

Low-carbon steel

It's known as mild steel. This type of steel contains less than 0.25% carbon and it is the most produced one. This steel is soft and weak but has exceptional ductility and toughness and it is the cheapest steel to produce but it has a weak corrosion resistance **[69][75]**.

There is a group of low-carbon alloys called high-strength, low alloys (HSLA). They have some others alloying elements (cupper, vanadium, nickel) that increase tensile strength, ductility and corrosion resistance **[69]**.

Medium-carbon steel

Medium-carbon steels contains carbon between 0.25-0.6%. These alloys have low hardenability and good ductility, strength and wear resistance but they have low resistant to the corrosion **[69][75]**.

The addition of chromium, nickel and molybdenum improve the strength and ductility of the steel.

High-carbon steel

High-carbon steels have carbon content of 0.6-1.4 %. These steels are the hardest, strongest and less ductile of the three carbon steels, they are also wear resistant but they still have low corrosion resistance **[69][75]**

Stainless steel

Stainless steels are iron-base alloys that have chromium as their major alloying element with concentrations higher than 11%. This chromium reacts with oxygen and moisture in the environment to form a protective, adherent and coherent chromium-rich oxide film that allows to

achieve the stainless characteristics. This film can repair itself when it is damaged thanks to the chromium in the steel that reacts with the oxygen in the environment to repair the oxide layer. Stainless steels are resistant to the corrosion and the resistance can be improve by adding nickel or molybdenum **[69][70][76][77][78]**.

Stainless steels are divided in three groups based on the microstructure at room temperature, these groups are **[69][76][77][78]**:

- Ferritic stainless steels, composed of α ferrite. They consist of iron and chromium (11.2-19 %) but without nickel or in a very small quantity.
  This type of stainless steel has good resistance to oxidation and better resistance to corrosion than martensitic stainless steel. Thermal properties are similar to conventional steels.
- Martensitic stainless steels, composed of martensite. They have higher carbon content (0.2-1 %) than the others to improve the strength and hardenability, chromium (10.5-18 %) and iron.
  Their corrosion resistance is moderate and the thermal properties are similar to conventional steels.
- Austenitic stainless steels, composed of austenite. It is the largest group of stainless steel, they consist of chromium (16-26%), nickel (6-12%) and iron. Molybdenum can be added to improve the corrosion resistance.
  They possess the highest corrosion resistance of all the stainless steels and they exhibit high thermal expansion and heat capacity but a lower thermal conductivity than other steels.
- Duplex stainless steels, composed of austenite and ferrite. This type consists of chromium (18-26 %), nickel (4-7 %), molybdenum (0-4 %), copper and iron.
  They have corrosion resistance, great strength and the thermal properties are similar to carbon steels.

The thermal properties of carbon steels and stainless steels (melting point and thermal conductivity) are compared next. It is difficult to establish a melting point and thermal conductivity for each type of steel because of the high variety of carbon and stainless steels.

In summary, the melting point of both steels are quite similar. The temperature range is between 1200-1500 ˚C. The Figure 16 shows the typical behaviour of the thermal conductivity of carbon and stainless steel in front of the temperature.

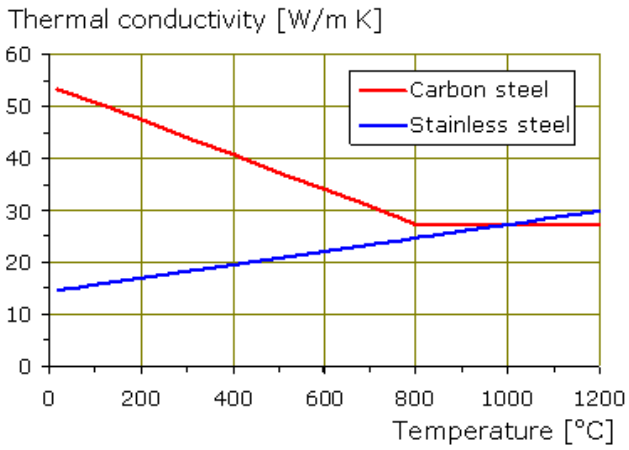

Figure 16. Thermal conductivity of stainless and carbon steel as a function of temperature **[79]**

Thermal conductivity of carbon steel is much higher than stainless steel at low temperatures but at high temperatures, stainless steel has better thermal conductivity.

Nowadays, the most common material to build a pyrolysis reactor is stainless steel as it is shown in Table 5 and 7, this is because stainless steel is a good heat conductive and it has a good chemical resistance. These properties are useful in a lab-scale reactor heated by a furnace.

As it is mentioned before, temperatures above 800 ˚C are necessary to produce biochar suitable for steelmaking industry **[15][16]**. The experiments showed before have mostly used stainless steel 316 with experiment temperatures up to 700 ˚C, this steel has a maximum service temperature of 800-900 ˚C, so in the case of this project this kind of material is not suitable **[80]**. But there are other types of stainless steel that can fit for purpose, for example the stainless steel 310 (C < 0.25, Cr 24-26, Ni 19-22, Mn < 2, Si < 1.5, P < 0.45, S < 0.3, Fe) with a melting range of 1400-1450 ˚C and a service temperature of 1100 ˚C. The chromium and nickel content makes it highly resistant to oxidation and corrosion. It is used in high temperature applications such as furnace parts and heat treatment equipment, combustors, kilns, retorts, muffles, among others **[81]**.

There is a special kind of alloys called superalloys that have excellent combination of properties and they are used in high temperatures applications and in oxidizing environments. It exists a brand named Inconel© from Special Metals Corporation that refers to a family of austenitic superalloys with a base of nickel and chromium **[82]**, three of them are list next.

- **Inconel 600** (Ni 72.0, Cr 15.5, Fe 8.0, Mn 1.0, C 0.15, Cu 0.5, Si 0.5, S 0.015) is a nickel-chromium alloy with a melting range of 1354-1413 ˚C and it has good oxidation resistance at higher temperatures and good resistance in carburizing and chloride containing environments. It is designed for being used at elevated temperatures around 1100 ˚C. The high nickel content gives resistance against reducing conditions and corrosion and the chromium content provides resistance to sulphur compounds and oxidizing environments. Inconel 600 is used in chemical and food processing, heat treating, phenol condensers among others **[83]**.

- **Inconel 601** (Ni 61, Fe Bal, Cr 23, Al 1.4, C 0.10, Mn 1.0, S 0.015, Si 0.5) is a nickel-chromium alloy with a melting range of 1360-1411 ˚C mainly used on applications that require resistance to heat and corrosion. The most important characteristic is resistance to oxidation at high temperatures up to 1250 ˚C, even under severe conditions such as heating and cooling cycles. It is also resistant to carburization. Inconel 601 is used in the fabrication of combustion chambers, thermal reactors in exhaust system of petrol engines, trays, baskets and fixtures in heat treatments… **[84]**

- **Inconel 625** (Ni 58.0, Cr 21.5, Mo 9.0, Mn 0.50, C 0.10, Si 0.50, Fe 5.0) is a nickel-chromium alloy with a melting range of 1290-1350 ˚C and a service temperature of 982 ˚C. The characteristics of the alloy make it a suitable material for sea-water applications, high corrosion-fatigue strength, high tensile strength and resistance to chloride-ion stress-corrosion cracking **[85]**.

Table 8 shows a selection of materials with their thermal properties and corrosion resistance.

Table 8. Thermal properties and corrosion resistance of metal alloys **[69][75][80][81][83][84][85]**.

Name	Type	Melting point (˚C)	Thermal conductivity ($W \cdot K^{-1} \cdot m^{-1}$)	Maximum Service Temperature (˚C)	Corrosion Resistance
AISI 1010	Carbon steel	1370-1400	54 (at 500 ˚C) 39 (at 800 ˚C)	500	Low

AISI 1095	Carbon steel	1515	51.9	125	Low
Stainless steel 310	Austenitic stainless steel	1400-1450	18.7 (at 500 ˚C)	1100	High
Stainless steel 316	Austenitic stainless steel	1375-1400	13 – 17 (at 500 ˚C)	750-925	High
Stainless steel 410	Martensitic stainless steel	1480-1530	23 – 27 (at 500 ˚C)	700-800	Medium
Inconel 600	Superalloy	1354-1413	22.1 (at 500 ˚C) 27.5 (at 800 ˚C)	1093	Very high
Inconel 601	Superalloy	1360-1411	19.5 (at 500 ˚C) 24.4 (at 800 ˚C)	-	Very high
Inconel 625	Superalloy	1290-1350	17.5 (at 538 ˚C) 22.8 (at 871 ˚C)	982	Very high

4.2.5. Pressure

4.2.5.1. Atmospheric pressure

Atmospheric pressure is the most common pressure used in pyrolysis reactors. It is easier and the auxiliary equipment is not needed so the cost is low and the system is not complex.

4.2.5.2. Pressurized pyrolysis

A reactor operated under pressure produces biochar and syngas yields higher than atmospheric conditions but it requires some extra equipment to pressurize the reactor.

4.2.5.3. Vacuum pyrolysis

This technique is useful to enhance the production of liquids. However, reactors that operate in vacuum conditions are more complex because of air leaks are not allowed.

4.2.6. Sealing

Vapours are generated during the pyrolysis process. The vapours and the temperature generate an overpressure inside the reactor, reason for what it is important to fix the lid of the reactor. It is also important to avoid any kind of leakage through the lid of the reactor. Several mechanism exist to prevent this and the most common are:

- Split-rings. These rings have the function of maintaining the lid of the reactor fixed. The ring is split into two sections and it clamps the head to the cylinder from the sides without interfering with anything connected to the head. There are two types of rings, without (Figure 17) and with screws (Figure 18). Screws are useful to bear higher pressures. If there are gases inside the reactor, the use of some sealing material between the head and cylinder of the reactor is advisable **[86][87]**.

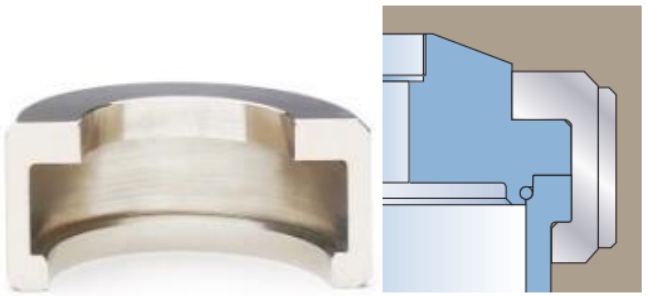

Figure 17. Split-ring for self-sealing O-ring closures **[86]**

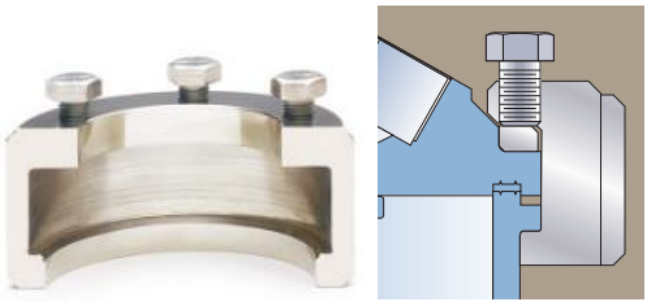

Figure 18. Split-ring with cap screws for removable vessels **[86]**

Some advantages of this rings are that the reactor can be opened and closed without removing any connections connected to the head, all the area on the head is available for attaching valves and accessories but it is only useful for moderate pressures **[86][87]**.

- Bolted closure. It consists of a head with some holes with thread that it is attached to the cylinder by screws (Figure 19). This mechanism resists higher pressures than rings but the opening and closing of the reactor is longer and not all the area on the head is available. It is normally used for high temperature reactions. If there are gases inside the reactor, the use of some sealing material between the head and cylinder of the reactor is advisable **[88][89]**.

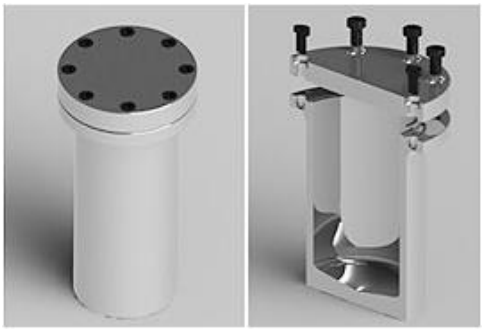

Figure 19. Bolted closure **[88]**

4.2.6.1. Sealing materials

Sealing materials for high temperature applications have to accomplish some characteristics. These are good bonding to the materials of interest, resistance to corrosion, low gas permeability and high heat conductivity **[90][91]**.

Graphite is the most common material used as a sealing material **[90]** but it starts to lose weight at about 125˚C and it maintains the seal up to 635˚C **[92][93]**. There are other materials that can work as a sealant such as aluminium oxide, tungsten carbide and silicon carbide but they are not suitable for high temperature applications **[90]**.

There is a compound based on sodium silicate and inorganic fillers that has high heat resistance, high degree of strength and excellent adhesion to metal surface. Moreover, it can resist temperatures above 1000 ˚C **[94][95]**. So, it is a suitable choice as a sealing material for reactors used in high temperature processes.

4.2.7. Process control

4.2.7.1. Observation of vapour colour

This control is used in carbonisation processes without heat or bio-oil recovery. The colour of the smoke gives information about what is happening in the reactor. White smoke indicates the

production of steam meaning that the drying of the biomass. Black smoke is related with the pyrolysis and after the pyrolysis has begun, the smoke turns more transparent.

4.2.7.2. Direct temperature measurement

It is important to control the temperature of the process due to the fact that the pyrolysis process depends on the temperature as well as the time. Thermocouple is an instrument that can be used for this purpose.

5. Vapours treatment

After the biomass pyrolysis, it is necessary to build a system to treat the outgoing vapours. These vapours are composed by a condensable and non-condensable part so the design of the system will determine the products that will be obtained.

Some experiments just release the vapours to the environment while others condense the vapours to produce bio-oil and store the non-condensable gases in a gas bag for further studies. The non-condensable gases can be also burned to produce heat for the reactor or other use.

5.1. Condensation

The condensation of the vapours leaving the reactor consists in cooling these vapours to recover the condensable fraction of the gases. This condensable fraction is known as bio-oil and it can be used as biofuel.

5.1.1. Condenser types

There are three types of condensers: air cooled, water cooled and evaporative.

- Air cooled condensers are used in small units like deep freezers, window air-conditioners, split air-conditioners… They are used in plants where the cooling load is small and they are normally made of copper or aluminium coil. They are also bigger than water cooled condensers. The operation mode can be natural convection and forced convection. In natural convection type, the air flows in a natural way depending on the temperature of the condenser while in the forced air type, a fan blows air through the condenser. **[96][97]**

  The simplest type of air condensers is a single tube where the vapour heat is conducted to the glass wall cooled only by air. These air condensers are often used for condensation of high boiling liquids. Other air condenser is the Vigreux column (Figure 20). It is a simple tube that includes downward-pointing indentations that increase the surface area per unit length of the condenser and the cost of the condenser. It is normally used in fractional distillation **[97]**. A Snyder column (Figure 20) is a high effective air cooled column used in selected fractional distillations, it consists of a single

glass with a series of circular indentations in the walls of the column where tear-shaped glass stoppers rest. These stoppers act as check valves, closing and opening with vapour flow and enhancing the vapour-condensate mixing. It is normally used as the fractionation column above a Kuderna-Danish concentrator, used to separate a low boiling solvent from high boiling volatile components **[98]**.

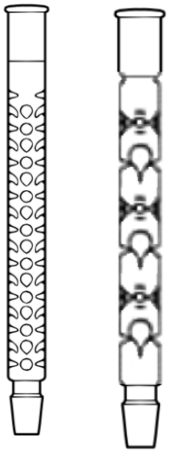

Figure 20. Vigreux and Snyder column **[96]**

- Water cooled condensers are used in large refrigerating plants where cooling loads are high and an elevated quantity of refrigerant flows through the condenser. There are three types of water cooled condenser: tube-in-tube or double pipe type, shell and coil type and tube type. The water flows through one side while the refrigerant flows to the other **[99]**.

  The Allihn condenser (Figure 21) is a tube-in-tube condenser that consists of a long glass tube with a water jacket. There are some bulbs that increase the surface area to facilitate the condensation. The Graham condenser (Figure 21) is a coil condenser that has spiral coil tube where the vapours condensate cover by a water jacket. The Dimroth condenser (Figure 21) is similar to coil condenser, it is formed by an internal double spiral where the coolant flows and the inlet and the outlet are both at the top. The vapours flow though the jacket from bottom to top. Finally, the Friedrichs condenser (Figure 21) is a spiral finger condenser that consists of an internal spiral cold finger-type tube inside a wide cylindrical housing. Coolant flows through the internal spiral while the vapours flwo through the housing, along the spiral finger **[96]**.

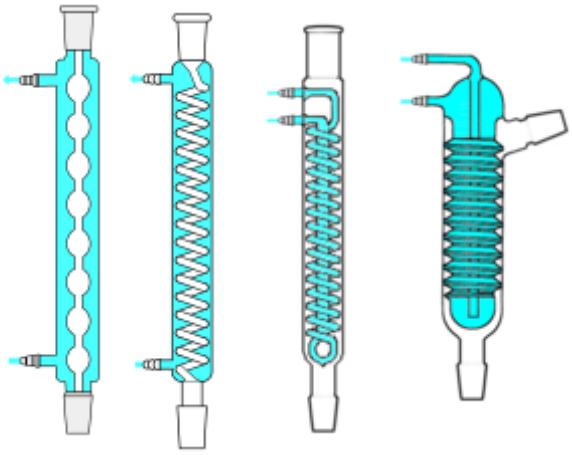

Figure 21. Allihn, Graham, Dimroth and Friedrichs condenser **[96]**

- Evaporative condensers are normally used in ice plants. They are a combination of the two types explained before, the hot refrigerant flows through the coils and the water is sprayed over them while, at the same time, the fan draws air from the bottom to the top. The water that comes in contact with the coil gets evaporated in the air and it absorbs the heat, cools the refrigerant and condense it **[99]**.

5.1.2. Connection glass-metal

Once the condensers have been seen, it is necessary to think about the connection between the metal pipe and the glass condenser. This connection has to join the two materials and seal the connection to avoid leakage.

There are a type of flanges made of 304 or 316L stainless steel that apply a uniform pressure from the clamp on the 15º surface of the flange. These flanges follow the ISO 2861 specifications **[100]**. Figure 22 shows a draw of a flange.

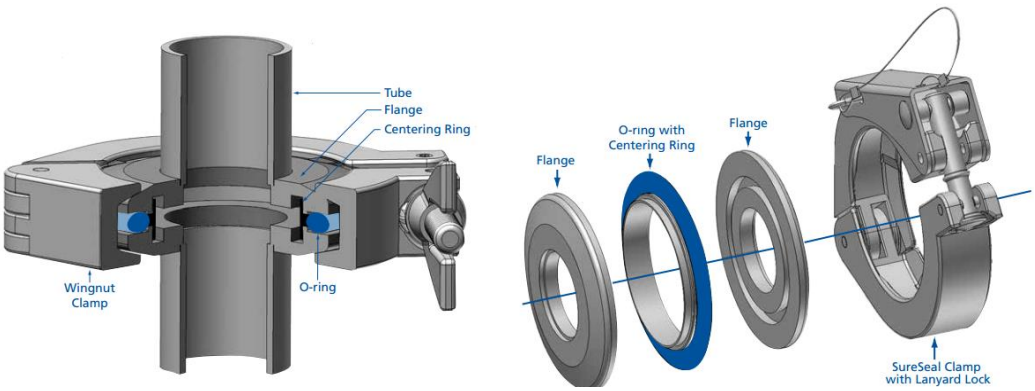

Figure 22. NW Flange **[100]**

5.1.3. Bio-oil condensation

Bio-oil is formed by different compounds that condensate at different temperatures so the condensation temperature has an important effect in the properties and composition of the resultant bio-oil. The heating value is higher for bio-oil condensing at lower temperature as well as the water content is lower from bio-oil collected at lower temperatures **[101]**.

So many options exist to condensate the condensable vapours, in the Table 9 are shown some of them.

Table 9. Condensation examples **[102]**

Description	Product Targeted
Pilot, 1st and 2nd: Water cooling jacketed condenser (1st at 100 ˚C and 2nd at 0 ˚C), 3rd: Filter	Tar and light liquids
1st: Hot water condenser; 2nd: Ice water condenser	Whole bio-oil
1st, 2nd, 3rd, 4th: Canisters in series inserted in a chilled batch with dry ice (1st: 275-351 ˚C, 4th: 50-75 ˚C) 5th: Electrostatic precipitator (ESP) at 30 kW	Whole bio-oil
1st and 2nd: Condensers with air cooling jacket, 3rd: ESP	Heavy and light oils and aerosols
1st, 2nd and 3rd: Condensers 4th: Air-cooled condensed 5th: Glass wool filled cartridge or ESP	Light oil Heavy oil Aerosol oil
1st Pipe bundle quencher at 300 ˚C, 2nd: Filter	Whole bio-oil

There are more articles with different systems to condense the vapours, for example:

- A water-cooled condenser (28-33 ˚C) followed by an ESP at 14 kW and two cold finger dry ice/acetone condensers to control the temperature below -70 ˚C, after theses condensers the non-condensable gases flow through a cotton wool filter for capturing some light compounds that may cross the condensers **[103]**.
- An ice-water bath at a temperature about 0 ˚C followed by a dry-ice/ethanol bath at 55 ˚C, finally the non-condensable gases are collected in a gas bag **[104]**.
- Two spraying condensers at 40-50 ˚C and 20 ˚C followed by a shell-tube-type cooler at 15 ˚C **[105]**.
- Two condensers, the first one is a hot water condenser at 60 ˚C and the second one is an ice water with NaCl condenser at -5 ˚C. The non-condensable are collected in a gas bag **[106]**.

5.1.4. Clogging problem

An important problem occurs inside the pipes after the gases leave the reactor and before they enter in the condenser, it is the clogging. It consists in the condensation of the vapours inside the pipe and causing a blockage, this obstructs the pass of the vapours. There are some ways to avoid the clogging such as heating the condenser inlet line to delay the condensation of vapours until they enter the condenser **[67][107]** and it is also possible to use a solvent to dilute the condensate. There are several compounds that can work as a solvent, some examples are listed next.

Benzene has a melting point of 5.4˚C and a boiling point of 80.1˚C. Benzene is insoluble in water but soluble in organic solvents and it is used in quick-drying, paint and varnish removers, coal tar solvent… The problem of this compound is that its vapours are toxic even in small quantity and it should be used only with ventilation **[108] [109]**.

Methanol has a melting point of -97.6˚C and a boiling point of 64.7˚C. It is used as an antifreeze, solvent, fuel… Methanol is miscible in water but its vapours are highly inflammable and toxic **[110]**.

Ethanol has a melting point of -114˚C and a boiling point of 78.37˚C. It is miscible in water, with many organic solvents and with light aliphatic hydrocarbons, it is a good general solvent. It is used in the purification of DNA and RNA due to polysaccharides precipitate in his presence. A disadvantage is that in some countries is considered a human drug so its use is restricted **[111][112]**.

Isopropanol has a melting point of -69˚C and a boiling point of 82.6˚C. The most common use for isopropanol is as a solvent for coatings or for industrial processes such as cleaning fluid for dissolving oils. It is miscible in water, benzene, chloroform, ethanol, acetone, salt solutions… and it dissolves a high quantity of non-polar compounds leaving null traces of oil, compared to ethanol and it is relatively non-toxic **[111][113][114][115]**.

Acetone has a melting point of -95˚C and a boiling point of 56˚C. It is miscible in water, benzene, diethyl ether, methanol, chloroform and ethanol. It is normally used as a solvent, for the production of methyl methacrylate and bisphenol A and it is a cleaner for the laboratory material. Acetone is a good solvent for many plastics and synthetic fibres **[116][117]**.

6. Heat transfer

The heat transfer is a science that studies the heat transfer between bodies at different temperatures. It can also predict the speed of this transfer under certain conditions. A simulation based on the heat transfer inside the reactor will be made to determine the reactor diameter.

There are three heat transfer methods: conduction, convection and radiation. The heat transfer inside the reactor will be considered as conduction supposing that the biomass is a solid body.

6.1. Heat transfer by conduction

When there is a temperature gradient in a body, there is a heat transfer from the high to the low temperature zone. This is known as heat transfer by conduction and it is represented as eq. 8 **[117]**:

$$q = -kA\frac{\partial T}{\partial x} \tag{8}$$

where q is the heat transfer speed, $\frac{\partial \mathrm{T}}{\partial \mathrm{x}}$ is the temperature gradient in the heat flow direction, k is the thermal conductivity of the material and A is the area. Taking the eq. 8 as the starting point it is possible to obtain the expression for the one-dimensional heat conduction in a body, supposing that the temperature can be changing through time and heat sources can exist, the eq. 9 is obtained **[118]**.

$$\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right) + \dot{q} = -\rho C_p\frac{\partial T}{\partial t} \tag{9}$$

where $\dot{q}$ is the generated heat, ρ is the density and C_p is the specific heat of the material. This equation can be expressed in different coordinate systems such as rectangular, cylindrical and spherical (eq. 10, 11 and 12) **[118]**.

rectangular $$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} + \frac{\dot{q}}{k} = \frac{1}{\alpha}\frac{\partial T}{\partial t} \tag{10}$$

cylindrical $$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{1}{r^2}\frac{\partial^2 T}{\partial \emptyset^2} + \frac{\partial^2 T}{\partial z^2} + \frac{\dot{q}}{k} = \frac{1}{\alpha}\frac{\partial T}{\partial t} \tag{11}$$

spherical $$\frac{1}{r}\frac{\partial^2}{\partial r^2}(rT) + \frac{1}{r^2 sen\,\theta}\frac{\partial}{\partial \theta}\left(sen\,\theta\frac{\partial T}{\partial \theta}\right) + \frac{1}{r^2 sen^2\,\theta}\frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} + \frac{\dot{q}}{k} = \frac{1}{\alpha}\frac{\partial T}{\partial t} \tag{12}$$

where $\alpha = k/(\rho \cdot C_p)$ and it is called thermal diffusivity.

6.2. Thermal conductivity

Thermal conductivity is the property of a material to conduct heat. Heat transfer across materials of low thermal conductivity happens at a lower rate than across materials with high thermal conductivity. This is why low thermal conductivity materials are used as insulators and high thermal conductivity materials are used in heat sink applications **[118]**.

Thermal conductivity is temperature dependant and it is measured in watts per meter kelvin in SI units. Table 10 shows the density and thermal conductivity of different biomass sources.

Table 10. Biomass density and thermal conductivity **[119]**

Biomass source	Density ($kg \cdot m^{-3}$)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
Sequoia	380	0.082
Pine	406	0.086
White wood	506	0.102
Cherry	534	0.108
White oak	615	0.113
Sewage sludge	760	0.130
Softwood	360	0.099
Pinewood	450	0.110
Spruce	400	0.128

7. HAZOP

A Hazard and Operability (HAZOP) study is an examination of a process or operation in order to identify and evaluate issues that can represent a risk for the equipment or the personal who operates it. In this case, the study has been done to determine possible system problems and correct them during the design process **[120]**.

A HAZOP study is composed of a system definition where the process is explained, the methodology of the HAZOP, the team members and the analysis of the main findings based on the tables where each component of the system is analysed.

7.1. System definition

A diagram of the system is shown in the Figure 23. The main parts of the system are the oven, the inlet and outlet pipe, the reactor and the condensers.

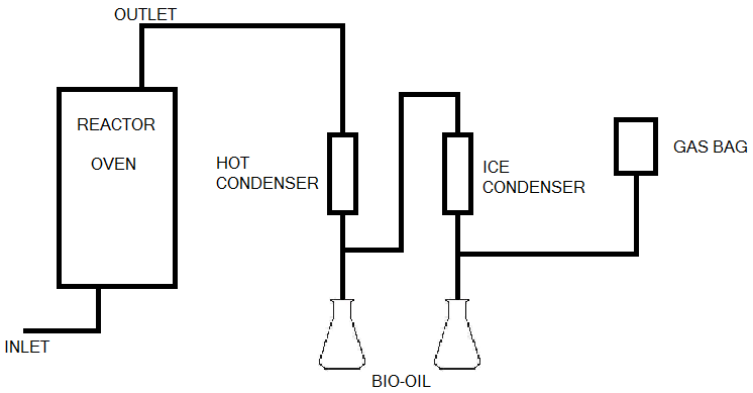

Figure 23. System diagram

Biomass is loaded inside the reactor and then the reactor is sealed. After, the reactor is placed inside the oven and closed. A nitrogen gas flow is introduced inside the reactor to expel the oxygen from the system. Once this is done, keeping the nitrogen flow during the experiment, the oven is turned on and the pyrolysis process starts. Biomass decomposes in biochar and vapours (non-condensable and condensable), these vapours exit the reactor through the outlet pipe and they cross two condensers, a hot condenser first and after an ice condenser, where the condensable fraction, bio-oil, is collected in a recipient while the non-condensable gases are collected in a gas bag. After the experiment is over, the oven is turned off and the cooling stage starts during 24 hours.

7.2. Methodology

For each plant item or node, relevant parameters and guide words for that node have been studied. The likely causes are in the third column and the consequences for these are in the fourth column. Where the consequences can have a potentially impact, possible changes to the system to eliminate or minimise the consequences were examined. These changes are presented in the sixth column while in the fifth there are the recommendation numbers.

7.3. Team members

Marc Sagrera

Gerrit Surrup

Johan Olav

Maximilian Kink

7.4. Analysis of main findings

These analysis are based on the tables 12, 13, 14, 15 and 16 that are placed in the Annex A.

Rec #1

Install a thermocouple to control the temperature. This controller allows to control the temperature inside the reactor and it gives the knowledge about if it is necessary to modify the temperature or not.

Rec #2

Increase the process duration to compensate the wrong thickness. If after the reactor design the thickness of the walls of the reactor results too big it is necessary to increase the duration of the process or the temperature to reach the desired conditions.

Rec #3

Control the process to ensure the operation time is the right one. It is important to reach the amount of time needed to convert the biomass into the products, for this a control of the time it is important.

Rec #4

Increase the diameter of the outlet pipe (design problem). This can be only modified during the design of the reactor. If the diameter is too small, the clogging could be favoured.

Rec #5

Clean the pipe with a solvent or a mechanical stamp to avoid the accumulation of the condensate inside the outlet pipe. The use of a solvent or mechanical stamp will facilitate the pass of the vapours and the no accumulation of the condensate.

Rec #6

Heat the pipe to avoid the clogging **[67][107]**. The heating of the pipe after the reactor will delay the condensation of the vapours.

Rec #7

Make the pipe go down to force the condensate to move down. If the pipe has the proper angle, bio-oil will go down and it will not accumulate and block the pipe.

Rec #8

Install a flowmeter to control the flow. It is important to know if the inlet and outlet flow are appropriate, the flowmeter will also be useful to detect if the pipes are blocked.

Rec #9

Check the volume flow at the beginning of the experiment (flash reactor for 5-10 minutes). It is important to check that the equipment works as it should.

Rec #10

Ensure that there is enough gas for the process and the cooling. Nitrogen gas is necessary to purge all the oxygen present in the system and to facilitate the heat transfer during the heating and the cooling stage.

Rec #11

Restart the experiment. If the pipe is blocked, the only solution is to clean it and restart the experiment.

Rec #12

Check the bomb before the experiment. It is important to check that the equipment works as it should.

Rec #13

Check the cooler. It is important to check that the equipment works as it should.

Rec #14

Install an adsorber after the condenser. If the condensable gases go through the condenser but they don’t condense, an auxiliary system is needed to retain them and avoid they flow to the gas bag.

8. System Design

8.1. Optimal process design parameters

Once the research has been done, it is time to choose the optimal parameters for the experimental part. The importance of these parameters is reflected on the characteristics of the products. Temperature, heating rate, residence time, particle size and nitrogen flow have been chosen to obtain a suitable biochar for smelting plants which means a fixed carbon content higher than 85%, volatile matter lower than 10% and low ash content.

Fixed carbon content and volatile matter are related with the experimental temperature but also with hemicellulose, cellulose and lignin composition of the biomass. Lignin compounds present higher biochar yield and higher fixed carbon content than hemicellulose and cellulose compounds and on the other hand, cellulose compounds present more volatile matter **[31][122]**. For a biomass with more lignin percentage, the biochar yield and fixed carbon content will be higher. Pinewood has a lignin content of 27%, it is not as high as the one from olive husk 48.4% or hazelnut shell 42.9% but pinewood is one of the most popular biomass source in Norway. From a former study it has been proved that olive husk can reach the 85% of fixed carbon content **[15]**, this project wants to test whether it is possible to achieve this percentage with pinewood.

In chapter 3.2.2., it has been talked about the required temperature. Based on two research articles **[15][16]** the temperature has to be higher than 800 ˚C to obtain this content. This can be related with the fact that cellulose and hemicellulose decompose for lower temperatures but the lignin is still remaining and with it a high fixed carbon content. The temperature range for the experiment will be from 700 ˚C to 1000 ˚C in order to keep the temperature of 800 ˚C inside the range and to observe the evolution of fixed carbon content from temperatures below to temperatures above of 800 ˚C. The only problem of using this temperature range is that the biochar yield will not be really high because the optimal temperature range to maximise the yield is from 300 ˚C to 600 ˚C **[29][34][35][36]**. A possible solution to increase the biochar yield is using a low heating rate. From chapter 3.2.3. it is known that the heating rate has to be low because the biochar yield decrease when the heating rate is increased. In Table 5 there are several experiments from researchers where the heating rate is shown. Based on those experiments, the heating rate will be between 5-10 ˚C/min because most of those experiments operate in this range and the condition of using a low heating rate is maintained.

The vapour residence time has been defined in chapter 3.2.6. and the value for this parameter has to be high because then vapours can react each other and produce more biochar **[7]**. It has been found that residence time for slow pyrolysis is normally around 5 seconds **[40]**. With this value and reactor area, that is defined later, the nitrogen flow can be calculated. The flow is related with the vapour residence time, the flow has to be small to generate high vapour residence time and favour the secondary reactions inside the reactor. The gas selected is used to expel all the oxygen from the system to run the pyrolysis and it needs to be inert, it cannot react with the biomass or the products formed. Normally, the gas used for this purpose is the nitrogen that it is used in some of the experiments showed in Table 5 **[56][57][59][61]**.

Finally, the particle size used in the experiments will be also defined later when the reactor dimensions will be defined. The particle size will be a downscaling of the particle size used in the Reichert retort. This downscaling will have the same magnitude as the reactor downscaling.

8.2. Reactor Design

8.2.1. Reactor type

Several actual industrial processes have been studied in order to choose and adapt one to produce biochar suitable for smelting plants. These processes are summarised in Table 4. Lambiotte reactor is one of the most efficient processes but it has the difficulty to reproduce the three zones of the industrial reactor in a laboratory. Other possible process is the auger reactor, although it can easily have a specific heating rate, it presents some disadvantages, for example: it is normally used to produce bio-oil by fast pyrolysis, the mechanical wear and the limitation of heat transfer at large scale that can cause problems when the lab-scale reactor is upgraded to industrial scale. Finally, the chosen reactor is the Reichert reactor because of the high biochar yield and its simplicity. There are not former experiments that can confirm that this is the best choice, so in part there is some risk in this selection.

The operation mode will be batch because of this is a lab-scale reactor heated up in an oven at atmospheric pressure and this mode is the most suitable and simple for lab-scale experiments. The reason is that the experiments will have different experimental conditions so the process will need to be stopped and restarted for each one of these conditions, batch.

The process is a slow pyrolysis of the biomass based on chosen heating rate (5-10 ˚C/min) and the reactor type will be fixed bed. As it is explained in chapter 4.2.1., fixed bed reactors are suitable for small-scale and they have long residence time and low gas velocity characteristics

that are necessary. On the other hand, the fluidised bed is normally used to produce bio-oil by fast pyrolysis.

8.2.2. Minimum reactor volume

To calculate the minimum volume it is necessary to know how much biochar is it required to produce in order to have enough mass to carry out the different analysis (ash content, volatile matter content, moisture content, carbon, hydrogen, nitrogen and sulphur total content). From the theoretical part it is possible to get the data necessary to do the calculations.

- Biochar yield by slow pyrolysis: 20-50%
- Mass needed for ash content analysis: 1 g
- Mass needed for volatile matter content analysis: 1 g
- Mass needed for moisture content analysis: 1 g
- Mass needed for carbon, hydrogen, nitrogen total content analysis: 1 g
- Mass needed for sulphur total content analysis: 1 g
- Pinewood bulk density: 202 kg·m^{-3} **[121]**

Minimum volume can be obtained following the eq. 13, 14 and 15. The worst case scenario (20% of biochar yield) is considered. The analysis have to be done three times so the mass is multiply by 3.

$$Minimum\ biomass\ for\ analysis = 3 \cdot (1+1+1+1+1)\ g \cdot \frac{1}{0.2} = 75\ g \quad (13)$$

$$Bulk\ volume = 75\ g \cdot \frac{1\ cm^3}{0.202\ g} = 371.3\ cm^3 \quad (14)$$

Normally the reactors are filled until the 80% of their capacity, so the minimum volume of the reactor is:

$$Minimum\ reactor\ volume = 371.3\ cm^3 \cdot \frac{1}{0.8} = 464.11\ cm^3 \approx 465\ \ cm^3 \quad (15)$$

The minimum reactor volume is 465 cm^3. This is the volume necessary to produce enough biochar mass to do the analysis. Considering that the reactor is a downscaling of a Reichert retort (8.5 m length and 5 m diameter), the minimum reactor radius is calculated in eq. 16, 17 and 18.

$$\frac{L}{r} = \frac{8.5}{2.5} = 3.4 \quad (16)$$

$$V = \pi \cdot r^2 \cdot L = 3.4 \cdot \pi \cdot r^3 \quad (17)$$

$$Minimum\ reactor\ radius = \sqrt[3]{\frac{V}{3.4 \cdot \pi}} = \sqrt[3]{\frac{465}{3.4 \cdot \pi}} = 3.67\ cm \quad (18)$$

8.2.3. Optimal reactor diameter

To obtain the optimal reactor diameter, a study of the temperature evolution through the pinewood in the reactor has been done for different diameters, between 5 and 10 cm. The starting point is the heat transfer equation for cylindrical coordinates but a few hypothesis are made to simplify the calculations.

- The heat transfer is calculated by conduction because of biomass is considered as a compact body.
- The heat transfer is one-dimensional in the radius direction.
- There is no heat generation in the body.
- It is only considered the transfer through the biomass and not through the walls of the reactor due to the big difference between their thermal conductivity (24.4 and 0.11 $W \cdot m^{-1} \cdot K^{-1}$).
- The body is symmetric respect the centre.
- The external biomass is next to a body with the reactor temperature.
- The initial temperature of biomass is 25 ˚C.

If all these hypothesis are applied to eq. 11, the remaining equation is the 20.

$$\frac{1}{\alpha}\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} \quad (19)$$

$$\frac{\partial T}{\partial t} = \frac{k}{\rho \cdot C_p}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) \quad (20)$$

The simulation has been done in MATLAB and the two functions used are in the Annex B. It consists in divide the radius in several differentials of temperature and calculate the temperature of these differentials in an exact moment of time. To do this, the eq. 20 needs to be transformed using Taylor's series and the eq. 21 is obtained.

$$\partial T(i) = \frac{k}{\rho \cdot C_p}\left(T(i+1) - 2 \cdot T(i) + T(i-1) + \frac{1}{r}(T(i+1) - T(i-1)\right) \quad (21)$$

Where T(i) is the temperature in the position i.

After the simulation a graphic of temperature in front of time is represented for each diameter. The minimum and maximum temperature has been studied (700, 1000 ˚C) and the temperature evolution has been done for 8 different positions inside the reactor. A scheme of the reactor divisions is shown in Figure 24 where number 1 is the centre of the reactor.

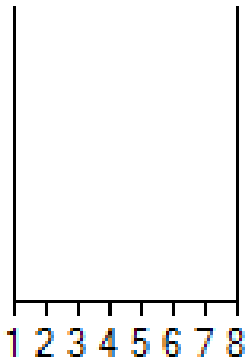

Figure 24. Reactor division scheme

Figure 25, 26, 27 and 28 show the evolution of the temperature through time for different reactor diameters and temperatures.

- Centre of the reactor: 700 and 1000 ˚C.
- 5/7 of the reactor radius (position 6): 700 and 1000 ˚C.

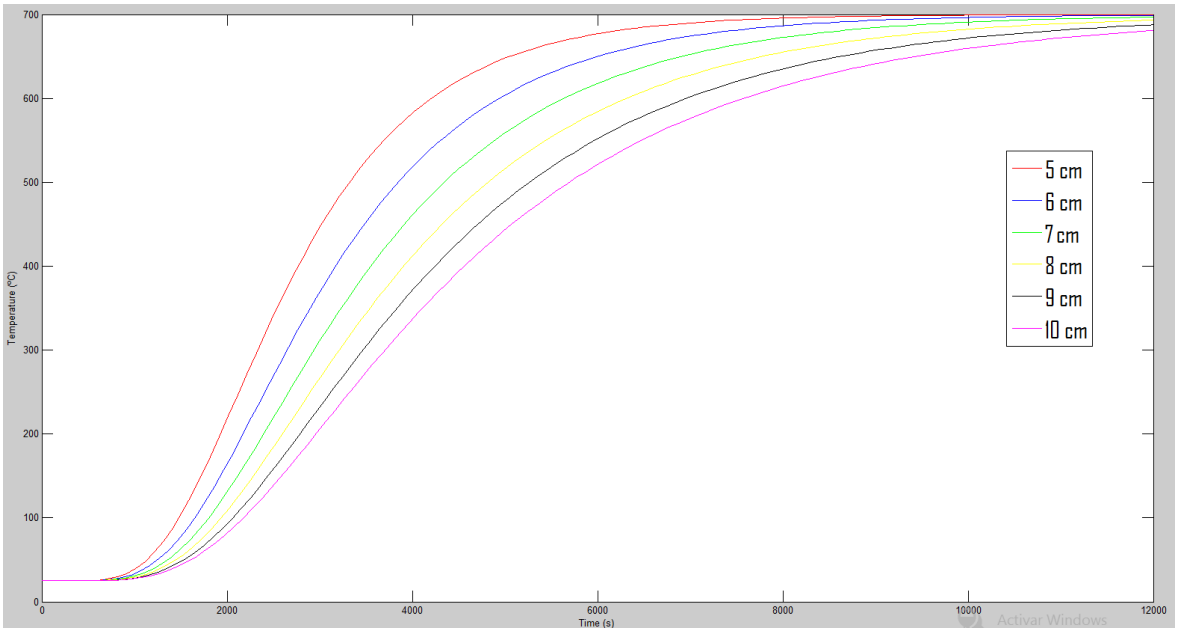

Figure 25. Temperature evolution through time in the centre of the reactor for an oven temperature of 700 ˚C and for different reactor diameters.

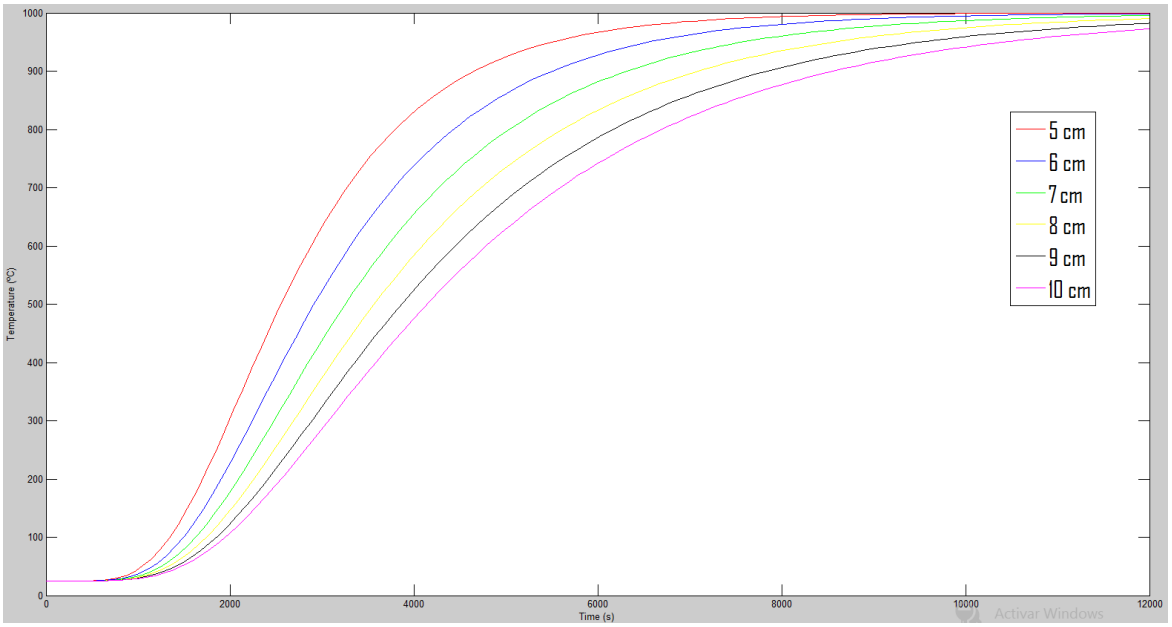

Figure 26. Temperature evolution through time in the centre of the reactor for an oven temperature of 1000 ˚C and for different reactor diameters.

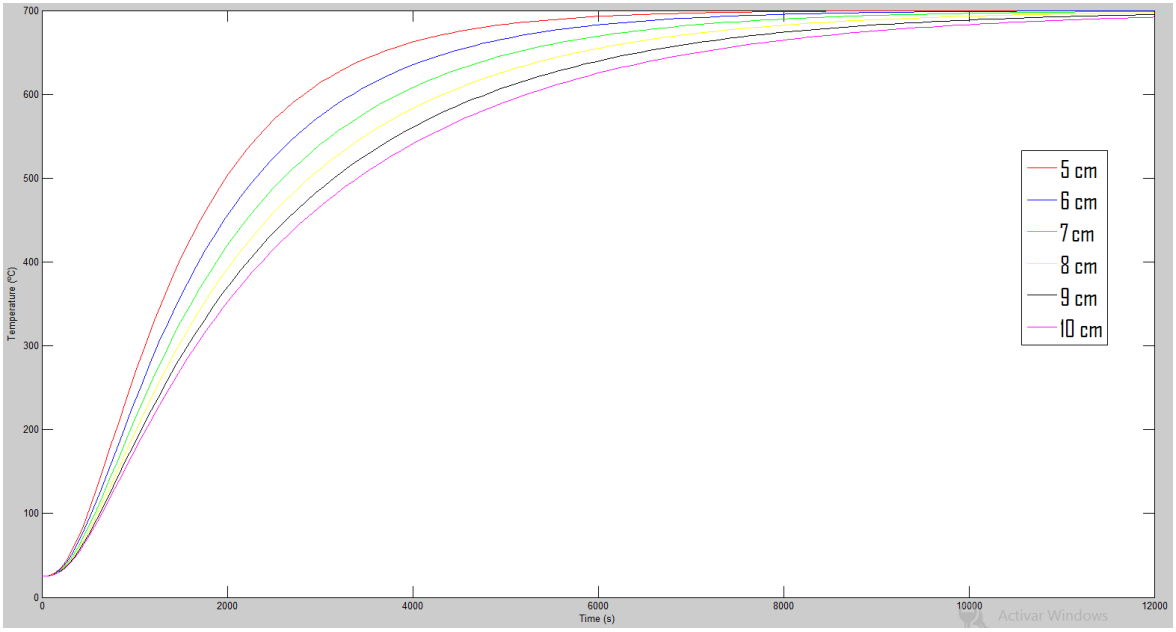

Figure 27. Temperature evolution through time in the 5/7 of the reactor radius and oven temperature of 700 ˚C for different diameters.

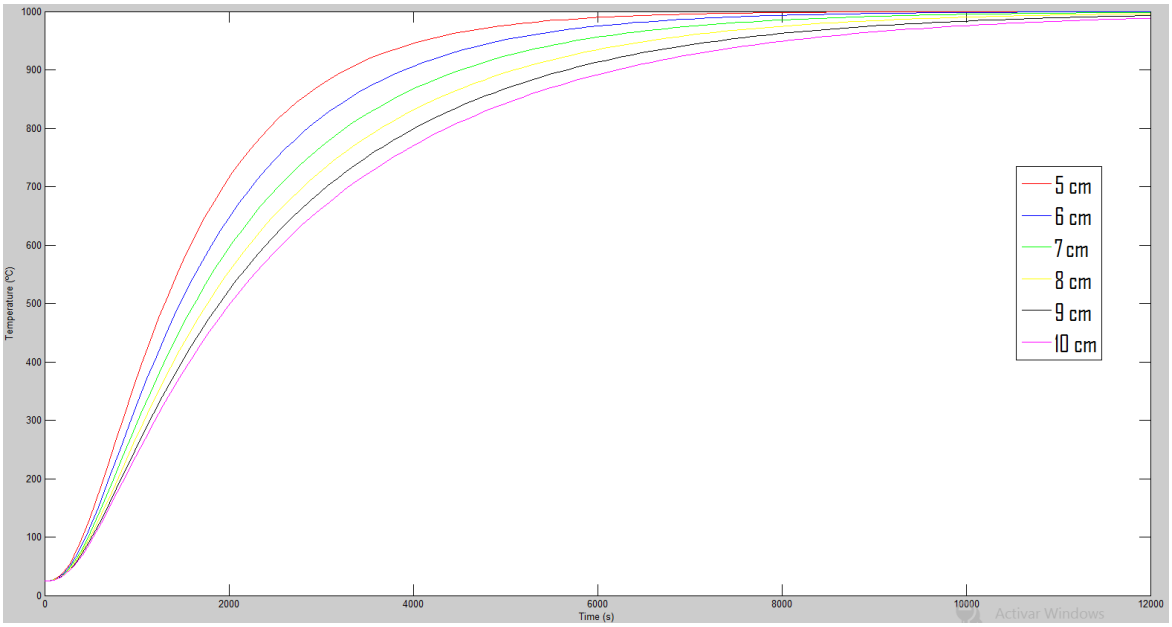

Figure 28. Temperature evolution through time in the 5/7 of the reactor radius and oven temperature of 1000 ˚C for different diameters.

The heating rate is obtained from the linear region of the graphs, it is calculated dividing the increase of the temperature by the increase of time for each time step and then the average heating rate from this section is calculated. Table 11 shows the heating rate obtained inside the reactor in different positions.

Table 11. Heating rate for different reactor diameters, temperatures of 700 and 1000 ˚C and different reactor positions.

Diameter (cm)	Temperature (˚C)	Heating Rate (˚C /min)								
		Centre	1/7 radius	2/7 radius	3/7 radius	4/7 radius	5/7 radius	6/7 radius	Radius	Average
5	700	6.70	6.86	6.89	7.09	7.48	8.35	10.09	11.02	8.06
6		6.26	6.47	6.52	6.76	7.16	8.10	9.88	10.89	7.76
7		5.81	6.05	6.13	6.41	6.89	7.85	9.66	10.76	7.45
8		5.38	5.65	5.76	6.07	6.60	7.60	9.46	10.64	7.15
9		5.00	5.27	5.42	5.76	6.34	7.38	9.29	10.53	6.87
10		4.65	4.93	5.11	5.48	6.09	7.17	9.12	10.44	6.62
5	1000	9.84	10.21	10.24	10.63	11.34	12.87	16.25	19.73	12.64
6		9.06	9.49	9.58	10.03	10.82	12.41	15.84	19.46	12.08
7		8.28	8.75	8.90	9.41	10.28	11.96	15.46	19.22	11.53
8		7.57	8.05	8.27	8.83	9.78	11.53	15.10	19.00	11.02
9		6.93	7.42	7.69	8.30	9.31	11.13	14.76	18.78	10.54
10		6.37	6.86	7.18	7.84	8.89	10.77	14.45	18.58	10.12

As it is shown in the Table 11, the heating rate decreases, when the diameter of the reactor increases. Another trend is observed, the values for the heating rate are higher for high temperature and for an external position.

To select the optimal diameter it has to be considered the minimum reactor radius calculated before (3.67 cm) and the heating rate value defined before (5-10 ˚C/min). Taking these two aspects into account the optimal diameter is 9 cm because the centre will have as a minimum heating rate the value of 5 ˚C/min and the maximum average heating rate will be of 10.54 ˚C/min at 1000 ˚C. Using the relation $\frac{L}{r} = 3.4$ from the industrial reactor size **[41]**, the reactor length is 15.3 cm. So the downscaling from the Reichert retort is around 56 times smaller. The thickness of the wall will be about 3 mm which is normally used and it is enough distance to allow the heat transfer through the wall.

The particle size is downscaled with the same magnitude as the reactor, considering that the particles used in the industrial process are 30 cm length and 10 cm thick **[41]**, the ones used in these experiments will be 0.54 cm length and 0.18 cm thick.

The nitrogen flow will be determined using the residence time, superficial velocity and reactor dimensions. Residence time has been defined as greater than 5 seconds and the reactor length is 15.3 cm so the superficial velocity of the gas is $v = \frac{15.3\ cm}{5\ s} = 3.06\ cm/s$ but taking in consideration the porosity of the biomass which it is 0.39-0.44 for pinewood the superficial velocity changes. The superficial velocity is calculated in eq. 22 and the maximum nitrogen flow in eq. 23.

$$v = 3.06 \cdot \frac{1}{0.39} = 7.85\ cm/s \tag{22}$$

$$Maximum\ Nitrogen\ flow = v \cdot A_R = 7.85 \cdot \pi \cdot 4.5^2 \cdot 0.39 = 53.3 \frac{cm^3}{s} = 3.2\ \frac{L}{min} \tag{23}$$

Where v is the superficial velocity, 0.39 is the porosity of pinewood and A_R is the reactor area.

Figure 29 shows a drawing of a possible design of the reactor. Inlet pipe is going to the bottom of the reactor while the outlet pipe is at the lid. The holes at the lid are for the screws and, finally, the other hole in the centre of the lid, next to the outlet pipe, is for the thermocouple.

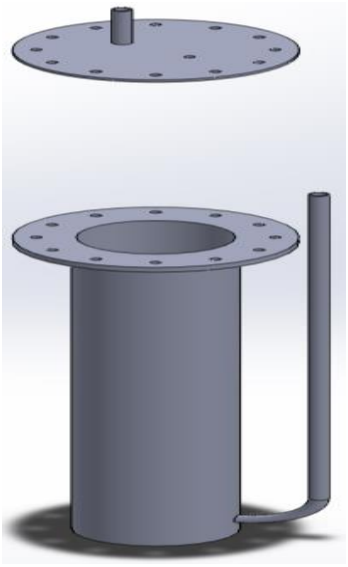

Figure 29. Reactor drawing

8.2.4. Reactor material

The material selected to build the reactor needs two important properties: a service temperature higher than 1000 ˚C and a good chemical resistance. The first property is because of the maximum experimental temperature, it is necessary a material than can bear a high temperature treatment without melting or losing its properties. A good chemical resistance is also necessary, it is important to resist the corrosion and low pH due to the vapours generated inside the reactor. The most common compounds of the vapours are acids, esters, phenols, sugars, aldehydes, ketones and alcohols that cause acid pH values.

Most of the experiments showed in Table 5 and 7 have stainless steel as a reactor material but in this project the experiment temperatures are up to 1000 ˚C and this material is not suitable for this conditions. After doing a material research, ceramics have been discarded because of their difficulty to produce and their fragility and breakability against hits.

Table 8 shows a summary of the metallic materials. Carbon steels are not useful because of their low chemical resistance and low maximum service temperature and although stainless steels have better chemical resistance their maximum service temperature are below 1000 ˚C that it is not enough. Finally, the superalloys (Inconel) have a quite high chemical resistance as well as high maximum service temperature. Inconel 600 (Ni 72.0, Cr 15.5, Fe 8.0, Mn 1.0, C 0.15, Cu 0.5, Si 0.5, S 0.015) and Inconel 601 (Ni 61, Fe Bal, Cr 23, Al 1.4, C 0.10, Mn 1.0, S 0.015, Si 0.5) are two superalloys that can be suitable as a reactor material.

8.2.5. Reactor lid closure

To avoid any leakage through the lid, two ways to fix the lid were studied, split-rings and bolted closure. The bolted closure is better than the split-rings, it is used in high temperature processes and can hold higher pressures **[86][87][88][89]**. It is necessary to fill the join between the cylinder and the lid with a sealing material. Due to the temperatures range, a compound based on sodium silicate and inorganic fillers is recommended on account of the characteristic that owns, high heat resistance, high degree of strength, excellent adhesion to metal surface and it can resist temperatures above 1000˚C **[94][95]**.

8.3. Vapours treatment system design

Finally, the vapours treatment system is designed to recover the condensable gases (bio-oil) and the non-condensable gases. There are several treatments to recover the vapours, in Table 9 there are some explained. From Table 9 and trying to keep the system simple, the choice is using two condensers, the first one is a hot water Dimroth condenser at 60 ˚C and the second one is an ice water with NaCl Graham condenser at -5 ˚C where the light fraction will be condensed **[106]**. The first condenser is a Dimroth because the heavy fraction will be condensed here so it is necessary to have enough area to avoid the blockage. The light fraction will be condensed in the second condenser, Graham condenser guarantees more contact area to improve the condensation. The bio-oil fraction condensed in each condenser is collected in a flask, the first fraction will correspond to the heavy fraction of condensable vapours while the second will be the light fraction. After the two condensers, the gases are collected in a gas bag or analysed online.

It is recommended to fix the connection between the metal pipe and the glass condenser with the NW flanges. This mechanism is capable of keeping attach the two pieces and avoid the leakage by sealing the join by pressure **[100]**.

During the HAZOP study, the clogging problem has been treated. This problem can block the pipes and impede to carry out the experiment. Some solutions have been found.

- The outlet pipe will be heated up to 400 ˚C by an external electric heat source to avoid condensation before the first condenser **[58]**.
- The outlet pipe will have a negative slope to force, in case that condensation occurs, the condensate to go down, far from the reactor.

- A solvent will be circulated in the outlet pipe to dissolve the condensate and avoid the clogging problem.

Several solvents have been studied and isopropanol is a suitable solvent. Bio-oil is formed mostly by acids, esters, phenols, sugars, aldehydes, ketones and alcohols that are miscible in water and water is miscible in isopropanol. It is commonly used as a solvent for dissolving oils, this is an appropriate characteristic to avoid the formation of the clogging. To calculate the amount of isopropanol necessary to avoid clogging it is necessary to know the critical compounds that may cause a second face. There is a 14.6% of bio-oil composition on dry basis that it is unknown **[25]**, it is supposed that this percentage is naphthalene, one of the biggest compounds of the bio-oil. The solubility of naphthalene in isopropanol is 54.66 mg/ml **[123]** so the amount of isopropanol is calculated in eq. 24, 25 and 26.

$$Biomass = V_R \cdot 0.8 \cdot \rho = \pi \cdot 4.5^2 \cdot 15.3 \cdot 0.8 \cdot 0.202 = 157.3\ g \quad (24)$$

$$Bio - oil = Biomass \cdot 0.15 = 157.3 \cdot 0.15 = 23.6\ g \quad (25)$$

$$Isopropanol = Bio - oil \cdot 0.146 \cdot solubility = 23.6 \cdot 0.146 \cdot \frac{1\ ml}{0.05466\ g} = 63\ ml \quad (26)$$

Where V_R is the reactor volume, ρ is the pinewood density and solubility is the solubility of naphthalene in isopropanol.

Another problem has appeared in the HAZOP. If the condensable fraction is not all condensed in the condensers it is necessary to avoid that arrives at the gas bag. Due to this, before the gas bag is necessary to install an adsorber. This adsorber can be a cotton wool filter **[103]** to capture some light compounds that may exit the two condensers, an activated carbon filter **[107]** or a combination of both.

9. Risk factors

After all experimental parameters and reactor characteristics have been chosen, there are two aspects that may cause a deviation from the expected results. These factors are the feedstock and the reactor type.

The feedstock used in this project is pinewood because is one of the most common biomass source in Norway but it only contains a 27% of lignin content on a dry basis. As it is said before, lignin percentage is related with the fixed carbon content, higher lignin percentage results in higher fixed carbon content and biochar yield. Although the pinewood is not one of the biomass sources with higher lignin content, it may be enough to reach the desired fixed carbon content.

The other aspect is the reactor type. Several actual industrial processes are compared and Reichert retort is selected above the others. The reactor choice is based on biochar yield and simplicity and those aspects do not guarantee that the product requirements will be met because they do not influence the fixed carbon content and volatile matter. So this selection has an inherent risk with it. It is also important to remind that the biomass needs a moisture content below 20% so normally biomass will be dried first.

10. Conclusions

Nowadays, the methods used in the industry to produce biochar for smelting plants are not enough to reach the suitable biochar characteristics and properties. These properties are a fixed carbon content higher than 85%, a volatile matter content lower than 10% and a lower ash content. In order to know if an actual industrial process can be modified and adapted to produce this kind of biochar, a downscaling of Reichert retort has been done.

Regarding to the experimental conditions, it is necessary to introduce some changes to set up the system. Temperatures higher than 800 ˚C as well as heating rates between 5-10 ˚C/min are selected so the reactor requires a material that can hold these new conditions. Superalloys like Inconel 600 and Inconel 601 are recommendable to use as a reactor material.

But fixed carbon content and volatile matter are not only affected by temperature and heating rate. Biomass has an important role so that is why it is advisable to use a biomass source that is not scarce in lignin content due to the fact that higher lignin percentages allow higher fixed carbon content while cellulose produces more volatile matter.

After the process conditions and feedstock have been selected, a MATLAB function has been used to simulate the temperature profile inside the reactor for those experimental temperatures. The diameter has been chosen taking into the account the heating rate and the resulting value of 9 cm is the best choice. Particle size it is also downscaled with the same magnitude as the reactor.

It is also important to design a system to collect the bio-oil and the non-condensable gases that exit the reactor. Bio-oil can be condensed using a hot water condenser followed by an ice water with NaCl condenser. Bio-oil can be used as fuel and non-condensable gases can be analysed and collected. The biggest problem of this part is the clogging and it can be avoided applying heat at the outlet pipe, using a solvent to dissolve the tar and making the outlet pipe with negative slope.

When the process is finished, proximate and ultimate analysis of the biochar will give the answer to if Reichert retort can be used as a process to produce biochar for smelting plants. In case the results are positive some changes will be necessary for upscaling the process. This system uses an oven as a heating source, in the industrial process this will be substituted by hot gases. It will be necessary to restore the reactor to its original size as well as the particle size

and the system to recover the bio-oil and non-condensable gases will be modified. Non-condensable gases will be burned and the heat obtained will be recirculated to heat up the reactor. Another possibility is to work with multiple retorts and use the off-gases from one retort as hot gases for the next retort.

On the other hand, if the results are negative it is necessary to check the system. For example, check if the temperature inside the reactor is the desired or if the feedstock is suitable for this process. To check the problem of the feedstock, olive husk could be used as feedstock because in a former study it has been proved that this kind of biomass reaches fixed carbon content values higher than 85%. If nothing of these have effect, it may be a problem of the reactor type and other studies should be done for different reactors like auger reactor.

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Annex A. HAZOP tables

Table 12. Reactor HAZOP table

Project: Biomass Pyrolysis					Table 12
Node: Reactor					Date: 19/05/2016
HAZOP team: Marc Sagrera, Gerrit Surrup, Johan Olav, Maximilian Kink					
Process Parameter	Guide Words	Possible Causes	Possible Consequences	Rec#	Recommendation
Temperature	Less	Oven malfunction	The final product is not the expected	1	Install a thermocouple to control the temperature
		Thickness of the wall is not appropriate	The final product is not the expected	2	Increase the process duration or temperature to compensate the wrong thickness
	More	Oven malfunction	The final product is not the expected	1	Install a thermocouple to control the temperature
		Thickness of the wall is not appropriate	The final product is not the expected	2	Increase the process duration or temperature to compensate the wrong thickness
Time	Less	Bad control	The final product is not the expected	3	Control the process to ensure the

					operation time is the right one
	More	Bad control	The final product is not the expected	3	Same as above
Pressure	More	Outlet is blocked (clogging)	Explosion risk	4	Increase the diameter of the outlet pipe (design problem)
				5	Clean the pipe with a solvent or a mechanical stamp to avoid the accumulation of the condensate inside the outlet pipe
				6	Heat the pipe to avoid the clogging **[67][107]**
				7	Make the pipe go down to force the condensate to move down
		Inlet flow is too high	Explosion risk	8	Install a flowmeter to control the flow
				9	Check the volume flow at the beginning of the experiment (flash reactor for 5-10 minutes)
				10	Ensure that there is enough gas for the process and the cooling
Flow	Less	Inlet pipe is blocked	The final product is not the expected	11	Restart the experiment
		Valve malfunction	The final product is not the expected	8	Install a flowmeter to control the flow

				9	Check the volume flow at the beginning of the experiment (flash reactor for 5-10 minutes)
				10	Ensure that there is enough gas for the process and the cooling
	More	Valve malfunction	The residence time is lower and the final product is not the expected		Same as above
	None	Valve is closed	Heat transfer is not the desired		Same as above

Table 13. Inlet pipe HAZOP table

Project: Biomass Pyrolysis					Table 13
Node: Inlet pipe					Date: 19/05/2016
HAZOP team: Marc Sagrera, Gerrit Surrup, Johan Olav, Maximilian Kink					
Process Parameter	Guide Words	Possible Causes	Possible Consequences	Rec#	Recommendation
Pressure	Less	Bomb malfunction	The final product is not the expected	12	Check the bomb before the experiment
	More	Pipe is blocked	The final product is not the expected	11	Restart the experiment
Flow	Less	Valve malfunction	The final product is not the expected	8	Install a flowmeter to control the flow
				9	Check the volume flow at the beginning of the experiment (flash reactor for 5-10 minutes)
				10	Ensure that there is enough gas for the process and the cooling
	More	Valve malfunction	The residence time is lower and the final product is not the expected		Same as above
	None	Valve is closed	The final product is not the expected		Same as above

Table 14. Outlet pipe HAZOP table

Project: Biomass Pyrolysis					Table 14
Node: Outlet pipe					Date: 19/05/2016
HAZOP team: Marc Sagrera, Gerrit Surrup, Johan Olav, Maximilian Kink					
Process Parameter	Guide Words	Possible Causes	Possible Consequences	Rec#	Recommendation
Pressure	More	Pipe is blocked (clogging)	Explosion risk	4 5 6 7	Increase the diameter of the outlet pipe (design problem) Clean the pipe with a solvent or a mechanical stamp to avoid the accumulation of the condensate inside the outlet pipe Heat the pipe to avoid the clogging Make the pipe go down to force the condensate to move down
Flow	Less More	Pipe is blocked (clogging) Excess of inlet flow	The final product is not the expected The residence time is lower and the final product is not the expected	 8	Same as above Install a flowmeter to control the flow

	None	Pipe is blocked (clogging)	The final product is not the expected Reactor pressure increase and there is risk of explosion		Same as “less” guide word Same as above

Table 15. Condenser HAZOP table

Project: Biomass Pyrolysis					Table 15
Node: Condenser					Date: 19/05/2016
HAZOP team: Marc Sagrera, Gerrit Surrup, Johan Olav, Maximilian Kink					
Process Parameter	Guide Words	Possible Causes	Possible Consequences	Rec#	Recommendation
Temperature	Less More	Cooler malfunction Cooler malfunction	The final product is not the expected The final product is not the expected	13 13	Check the cooler Check the cooler
Flow	Less	Pipe is blocked (clogging)	Obstruction in the condenser	5 7	Clean the pipe with a solvent or a mechanical stamp to avoid the accumulation of the condensate Make the pipe go down to force the condensate to move down

	More	Excess of inlet flow	Gases don’t condense	14	Install an adsorber after the condenser

Table 16. Oven HAZOP table

Project: Biomass Pyrolysis					Table 16
Node: Oven					Date: 19/05/2016
HAZOP team: Marc Sagrera, Gerrit Surrup, Johan Olav, Maximilian Kink					
Process Parameter	Guide Words	Possible Causes	Possible Consequences	Rec#	Recommendation
Power	Off	No electricity	The process doesn’t work		
Temperature	Less	Oven malfunction	The final product is not the expected	1	Install a thermocouple to control the temperature
	More	Oven malfunction	The final product is not the expected	1	Install a thermocouple to control the temperature

Annex B. MATLAB functions

The two functions used in MATLAB are written next.

```
function dT=cylinder(t,T)
%heat transport through the bulk
%dT/dt = m * (d2T/dr2 + 1/r * dT/dr)
%dT(i) = m * [T(i+1)-2*T(i)+T(i-1)+ 1/r * (T(i+1)-T(i-1))]
%m = k/(Cp*p)
m = 0.00177134;
radi = 5;
r = radi/7;
dT(1)= m*(2*T(2)-2*T(1));
for i=2:7
    dT(i)= m*(T(i+1)-2*T(i)+T(i-1)+1/(r*(i-1))*(T(i+1)-T(i-1)));
end
dT(8)=m*(1000-2*T(8)+T(7)+1/(r*7)*(1000-T(7)));
dT=dT';
end
```

Where m value is for pinewood and 1000 is the temperature of the oven. It is changed to 700 to simulate the other temperature process.

```
oset=odeset('MaxStep',100);
[t,T]=ode15s(@cylinder, [0 tm], [25 25 25 25 25 25 25 25], oset);
L=[t,T];
```

Where tm is the time in seconds you want to select and the 25s are the initial temperature of the biomass.